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Chromatographic determination of hydrocarbons based on retention time data for squalene and tetracyanoethylated pentaerythritol columns

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CHROMATOGRAPHIC DETERMINATION OF HYDROCARBONS BASED ON RETENTION TIME DATA FOR SQUALENE AND TETRACYANOETHYLATED PENTAERYTHRITOL COLUMNS

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A

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ABSTRACT

The purpose of this thesis is to investigate the theory that when several members of a homologous series are injected into a gas chromatograph, at a given flow rate and column temperature, the lograrithm of their retention time as a function of some increasing property of the homologous series may be presented as a straight line and to develop their equations.

Experimental procedure was accomplished for the normal paraffin series with 7½% squalene and 10% Tetracyanoethylated Pentaerythritol (T.C.E.P.E.) columns and the relation between retention time and carbon number was determined.

The same type of development was employed for aromatic compounds with a 10% T.C.E.P.E. column and the relation between retention time and boiling point of the compound was ascertained.

ACKNOWLEDGMENT

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I. INTRODUCTION

Chromatography is related to extraction and fractional distillation of hydrocarbon in that the components of a sample are distributed between two phases. The feature distinguishing chromatography from most other physical methods of separation is that one phase is stationary and the other is mobile. The moving phase can be either gas or liquid and the stationary phase can be liquid or solid.

Gas chromatography is a technique for separation of hydrocarbon components by percolating a gas stream over a stationary phase. If the stationary phase is a solid, the technique is known as gas - solid chromatography in which the separation of gases depends upon the adsorptive properties of the column packing.

Liquid chromatography occurs when the stationary phase is a liquid. The liquid is spread over the grains of an inert solid and the basis for separation is the partitioning of the sample through the liquid phase.

Chromatography appears to have had its beginning about 1850 when F.F. Runge[1] presented a paper known today as paper chromatography. Subsequently, Ramsey[2], Tswatt[3], Martin and Synge[4] have presented various experimental techniques to determine composition of unknown mixtures.

In recent years, great attention has been paid to the technique of separation by the works of James and Martin[5], Zlatkis[6], Eggertsen & Groennings[7], Polar, Holst and Grownnings[8], Durrett et al[9], and Desty and Goldup[10].

The petroleum engineer's primary concern is to know the compositions that exist in recovered crude oil and natural gas, and to be able to separate the entire range of products from light hydrocarbon gases up to waxes, and asphalts for commercial purposes.

The purpose of this investigation is to determine a mathematical relationship between the different components present and physically controlled variables, namely; operating flow rate and temperature. By determining the time required for peaks to appear on the chromatogram, compounds present in a mixture may be identified through the use of the equations developed.

II. LITERATURE REVIEW

In 1850 F.F. Runge[1], a German dye chemist, described a separation process known today as paper chromatography. Chromatography upon paper is one of the most important modern forms of the technique and probably the first to be discovered. There seems no doubt that the discovery sprang from an empirical practice in the dyeing industry. It was customary for workers to test the strength and quality of dye - baths by applying a drop of the liquid to adsorbent material, such as paper or cloth, and then observing the pattern of concentric rings, corresponding to different constituents in the dye, which formed as the liquid was drawn outwards by capillary action. Runge[1] recognized that the method need not be restricted to dyes and investigated in some detail its possibilities in inorganic analysis; he proved that many inorganic cations can be separated by virtue of the differences in their rate of migration when their solutions are drawn through paper or other porous materials by capillary action.

In 1905, chromatography was used by Ramsey[2] to separate mixtures of gases and vapors. In 1906 Tswett described the first form of column chromatography, now called liquid-solid elution chromatography, which he applied to the colored pigments from plant materials. The term "chromatography" was coined at this time and literally translated means color writing. Since Tswett's time, of course, column chromatography has been extensively applied to colorless materials so that

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1. References are given at end of paper.

today the name is somewhat inconsistent with the practice.

Martin and Synge[4] in 1941, in a paper dealing with liquid-liquid chromatography, for the first time specifically suggested gas-liquid chromatography in which the moving phase was called the carrier gas and the stationary phase was a liquid on a finely divided solid support packed into a column.

In spite of their suggestion, no application of the technique was developed until eleven years later when James and Martin[5] published their first paper dealing with the separation of volatile fatty acids. Since then no technique in analytical chemistry has been so quickly and widely adopted.

Three main factors have caused this explosive growth; first, in 1952, the obviously powerful technique of ion exchange and liquid-liquid chromatography laid the ground work for the acceptance of yet another chromatographic technique named gas-liquid chromatography; second, in 1952, methods of hydrocarbon analysis were cumbersome, time-consuming, and expensive; third, nonspecific detectors were developed that could respond to all eluted sample compounds and present chromatographic results in a form such as Figure 1.

In 1956 it was exciting to see the simple separation and measurement of a mixture of ethane, propane, and butane (Figure I). In 1958 Zlatkis[6] described the resolution of the isometric hexanes, and Eggertson and Groennings[7] the determination of the saturated hydrocarbons containing five to seven carbon atoms. In 1962, Polar, Holst, and Groennings[8] described the determination of alkanes through octane. In 1963 Durrett et al[9]. reported the determination of hydrocarbons

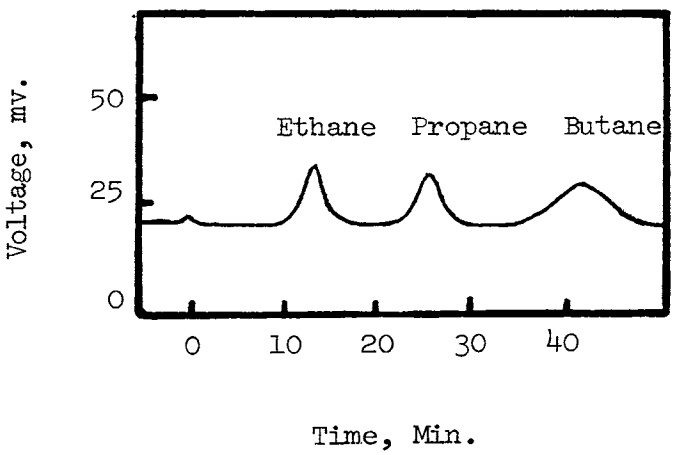

Figure (1). Separation of .05 ml (STP) of a Mixture of Ethane, Propane, and Butane on Silica Gel.

through nonane and the identification of some decane isomers. By the use of high-speed gas chromatography Desty and Goldup separated and measured a four-component mixture in one second, and the nine heptane isomers in less than a minute. The science and art of gas chromatography has today reached a high level of refinement and previously extravagant dreams continue to become realities.

III. EQUIPMENT AND EXPERIMENTAL CONDITIONS

A. Equipment

The gas-chromatograph used in this experiment, Model A-700, "AUTO PREP," Figure 2 and Figure 3 which is equipped with a thermal conductivity detector, employs the following components:

1. Column:

A column which contains the stationary phase and can be as long as 100 feet with a small diameter. Gas-liquid chromatography utilizes a liquid phase that must be stable and non-volatile at column temperatures and is spread as a thin film on a "solid support" which is either a granular solid in a packed column or the inner wall of capillary column.

2. Carrier Gas:

A carrier gas, or eluent gas which acts as the mobile phase flowing through the column to support sample components from the injection point to the detector.

3. Sample Injector:

A sample injector by which the sample is injected into the carrier gas stream before it enters the column.

4. Detector:

A detector which indicates the presence and amount of solute in the carrier gas stream. The thermal conductivity (T.C.) detector employs a tungsten filament which is kept at a particular temperature by passing a constant current through it. Carrier gas flows over the filament and dissipates heat at a constant rate. When sample molecules mixed with carrier gas pass over the hot filament, the rate of heat loss is reduced and the resistance of the filament increases; this change in resistance causes a voltage change at a constant current which is measured with a

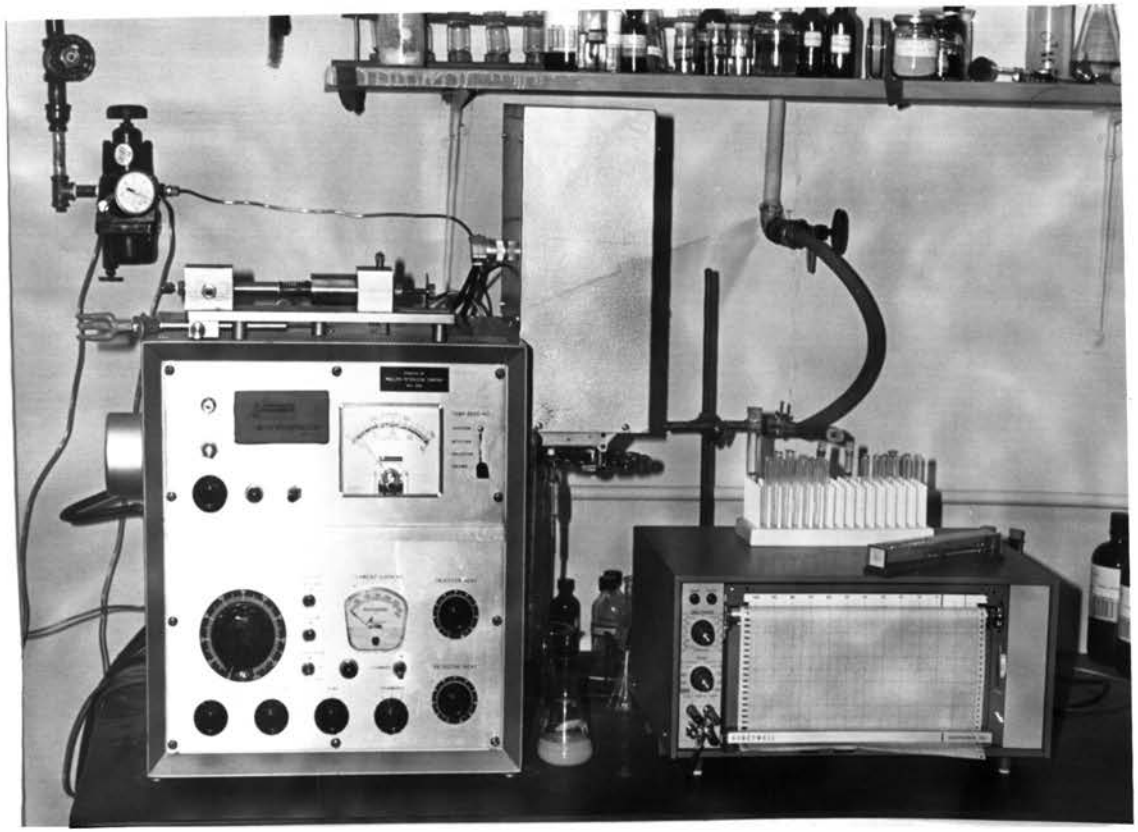

Figure (2). Gas Chromatograph Unit

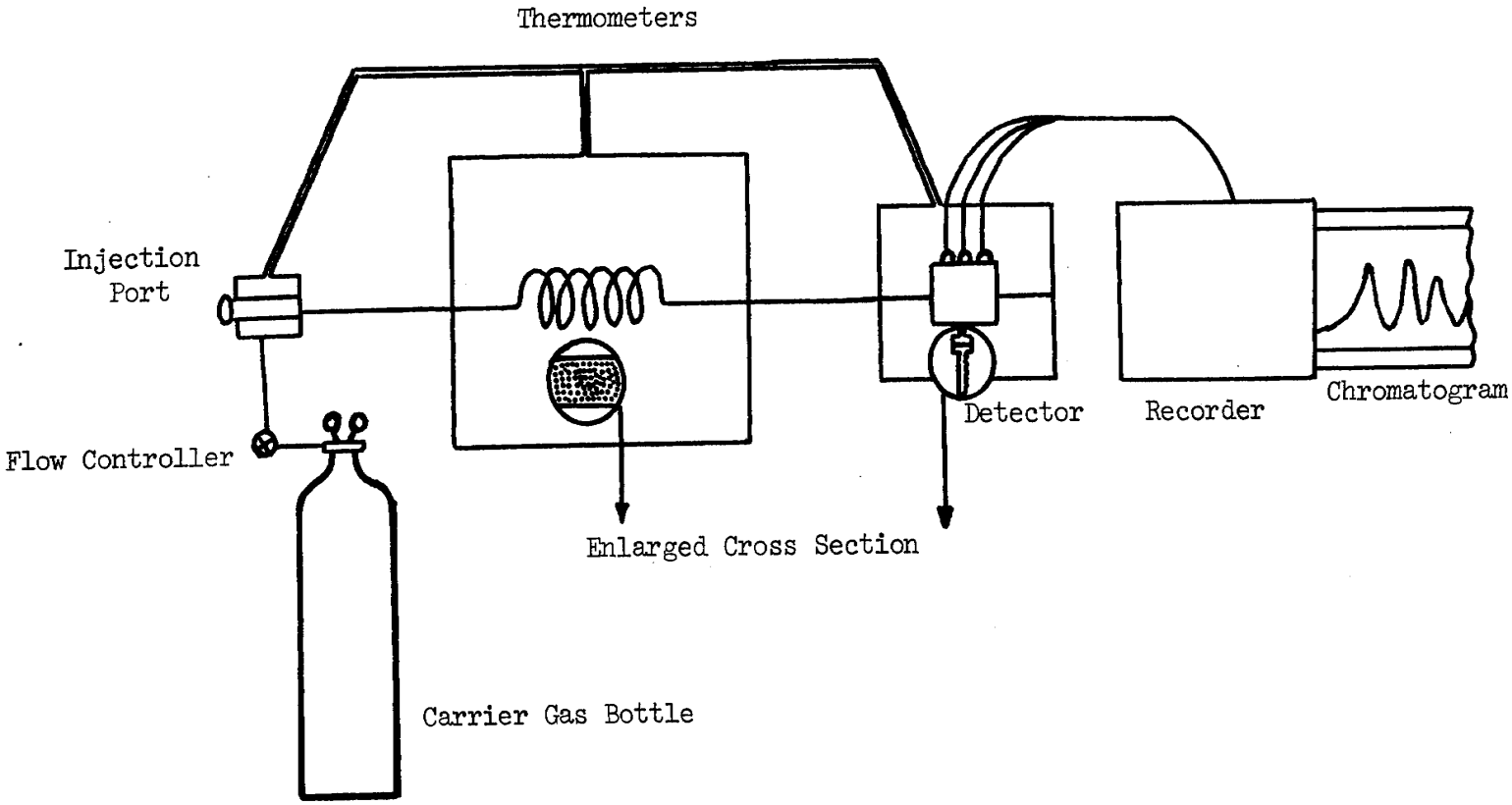

Figure (3). Schematic Drawing of a Gas Chromatographic System

Wheatstone Bridge and the signal fed to a recorder where it appears as peaks.

The heat is transferred by conduction when gas molecules strike the heated filament and rebound with increased kinetic energy. The greater the number of molecule collisions with the filament per unit time, the greater the rate of heat loss. Differences in thermal conductivity of gases are based on the speed at which the molecules diffuse. The speed of the molecules is a function of molecular weight, so the principle of operation is that the ability to conduct heat from a filament is a function of molecular weight of the gas.

5. Recorder:

A recorder which graphically illustrates the detector response as a function of time; this response is known as a chromatogram. This consists of a base line corresponding to emergence of pure carrier gas and of peaks corresponding to emergence of the various components of the sample.

B. Experimental Conditions

In gas chromatography the aim is to obtain optimum peak separation and narrow peaks; successful separations in chromatography result from the correct choice of a column, stationary phase, carrier gas and its flow rate, sample introduction, detector and the operating temperature of the column, detector and injector.

1. Column:

The success or failure of a particular separation depends on the choice of the column, since the column is the heart of the chromatograph and the actual separation occurs in the column. Lengthening a column will increase the separation but too lengthy of a column is impractical to use which is why a 15 foot folumn was employed in the

experiment. Straight columns are more efficient but may be impractical at high temperatures; also they require a very high inlet pressure. If they are coiled, the spiral diameter should be at least ten times the column diameter to minimize diffusion.

The liquid phase used in gas-liquid chromatography must be stable, non-volatile at column temperature, and show appropriate solubility for sample components. The liquid used in the experiment was squalene or tetracyanoethylated pentaerythritol which had the mentioned specifications.

The solid supports should be inert, small and of uniform mesh size. The support used in the experiment was Chromosorb P (Pink); Grades are prepared from Johns ManVille C-22 firebrick which provides the highest column efficiency.

2. Carrier Gas:

In gas-liquid chromatography, the choice of a carrier gas is not as critical as in gas-solid chromatography. Impurities in the gas are more critical in gas-liquid chromatography. A high pressure regulator is used to assure a uniform input pressure of 55 psig and results in a constant rate of gas flow.

The carrier gas should be inert in order not to react with the sample, readily available, inexpensive, pure, and suitable for the detector used. Helium is suitable for thermal conductivity detectors as the signal from a T.C. cell depends on the difference between the thermal conductivity of the solute vapor and carrier gas.

3. Sample Introduction:

The sample introduction should be instantaneous from a microliter syringe through a rubber septum. The sample should be carried as a vapor to the end of the column in negligible time. The sample size should be small, .005 ml to .01 ml, and injection temperature high enough to prevent condensation.

4. Detector:

The detector has a high sensitivity when its filament is in operation at high current, 150 milliampere, the carrier gas used has a high thermal conductivity, and the flow rate is low. The detector temperature should be higher than the column so that condensation of both solutes and liquid phase in the cell is avoided.

a. Injection port temperature:

The injection port temperature should be high enough to cause an instant vaporization of the sample so that no loss in efficiency results, and should be low enough not to cause any thermal decomposition or rearrangement. A practical test is to raise the temperature and notice if the shape of the peaks improve, if so the temperature is too low, on the contrary if the shape of the peaks changes drastically, the temperature is too high causing decomposition or rearrangements.

b. Column Temperature:

The column temperature should be high enough so that the analysis takes place in a reasonable length of time, and low enough that the desired separation is obtained.

c. Detector Temperature:

The detector must be hot enough to prevent any condensation of the vaporized sample in the column. Peak broadening and loss of component peaks are characteristics of condensation.

IV. RESULTS

A. Normal Paraffins - Squalene Column

Since the normal paraffin and aromatic compounds are normal constituents of any crude oil sample, their identification is a matter of some commercial importance. The liquid used in first part of the experiment is a combination of normal pentane, normal hexane, normal heptane, and normal octane.

The sample size varied from 0.005 to 0.01 milliliters, and the injection port was kept at a constant temperature of 155°C. The column used for this determination was 3/8" O.D. x 15 ft of 7 1/2% Squalene on Chromosorb "P", with a maximum temperature of 125°C. The detector temperature remained at 210°C during experimentation.

The samples were run at column temperature of 50,60,80,100°C, and flow rates of 100,120,140,160,200 CC/min. Three samples were run for each value of flow rate and the average value of retention time was found from the chromatograms. Tables 1 through 4 shows the data obtained. By plotting the retention time versus the carbon number on semilog graph paper, a series of parallel straight lines, Figure 4 through 7, resulted. Equations to be used for identification of unknown samples of normal paraffin series when their retention times are known at the operating temperature and flow rate were then determined. This was accomplished by employing the method of averages to find the constants 'A' and 'B', the slope, the 'y' intercept, in the Equation 1.

$$*tr = e^{A+BC} \qquad (1)$$

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* Nomenclature is given in Appendix A.

Table 1

Average Retention Time at 50°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave Ret. Time at 200 cc/min
C_5H_{12}	200.4	175.2	157.2	144.0	118.8
C_6H_{14}	558.0	487.20	445.2	398.4	324.0
C_7H_{16}	1498.8	1315.20	1210.8	1098.0	891.6
C_8H_{18}	4161.6	3621.60	3322.8	3001.2	2343.6

Table 2

Average Retention Time at 60°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	152.4	130.8	120.0	108.0	91.2
C_6H_{14}	398.4	343.2	313.2	280.8	242.4
C_7H_{16}	1017.6	888.0	805.2	724.8	628.8
C_8H_{18}	2640.0	2247.6	2092.8	1867.2	1645.2

Table 3

Average Retention at 80°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	91.8	79.8	69.6	56.4	48.0
C_6H_{14}	220.2	190.2	163.8	134.4	114.6
C_7H_{16}	518.4	447.0	387.0	316.2	270.6
C_8H_{18}	1213.2	1046.4	954.0	740.4	634.2

Table 4

Average Retention at 100°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	57.6	50.0	42.8	41.2	35.2
C_6H_{14}	126.4	110.4	94.4	90.8	79.2
C_7H_{16}	275.2	240	205.6	198.0	172.4
C_8H_{18}	597.2	519.6	444.4	428.4	373.2

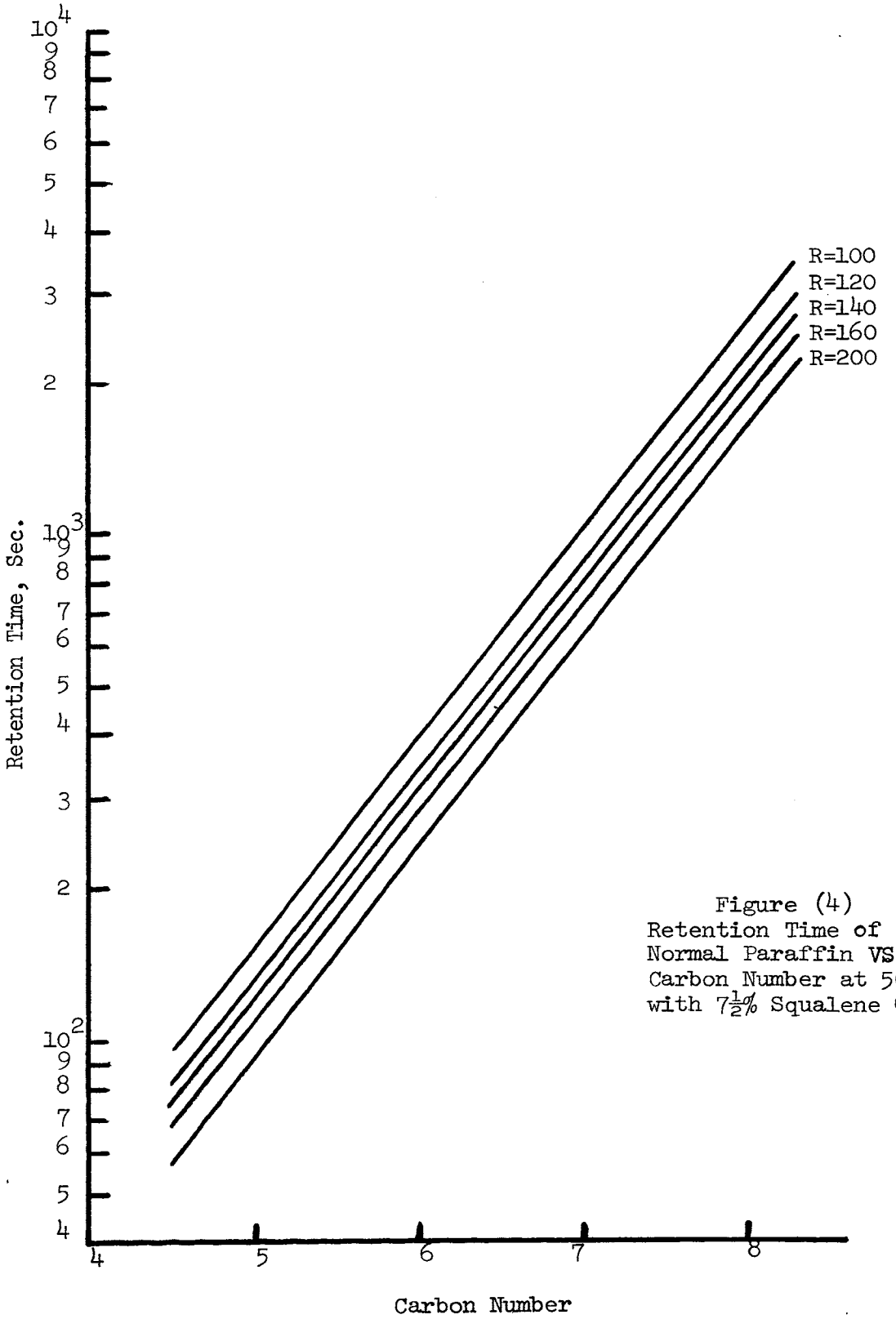

Figure (4)
Retention Time of
Normal Paraffin VS.
Carbon Number at 50°C
with 7½% Squalene Column

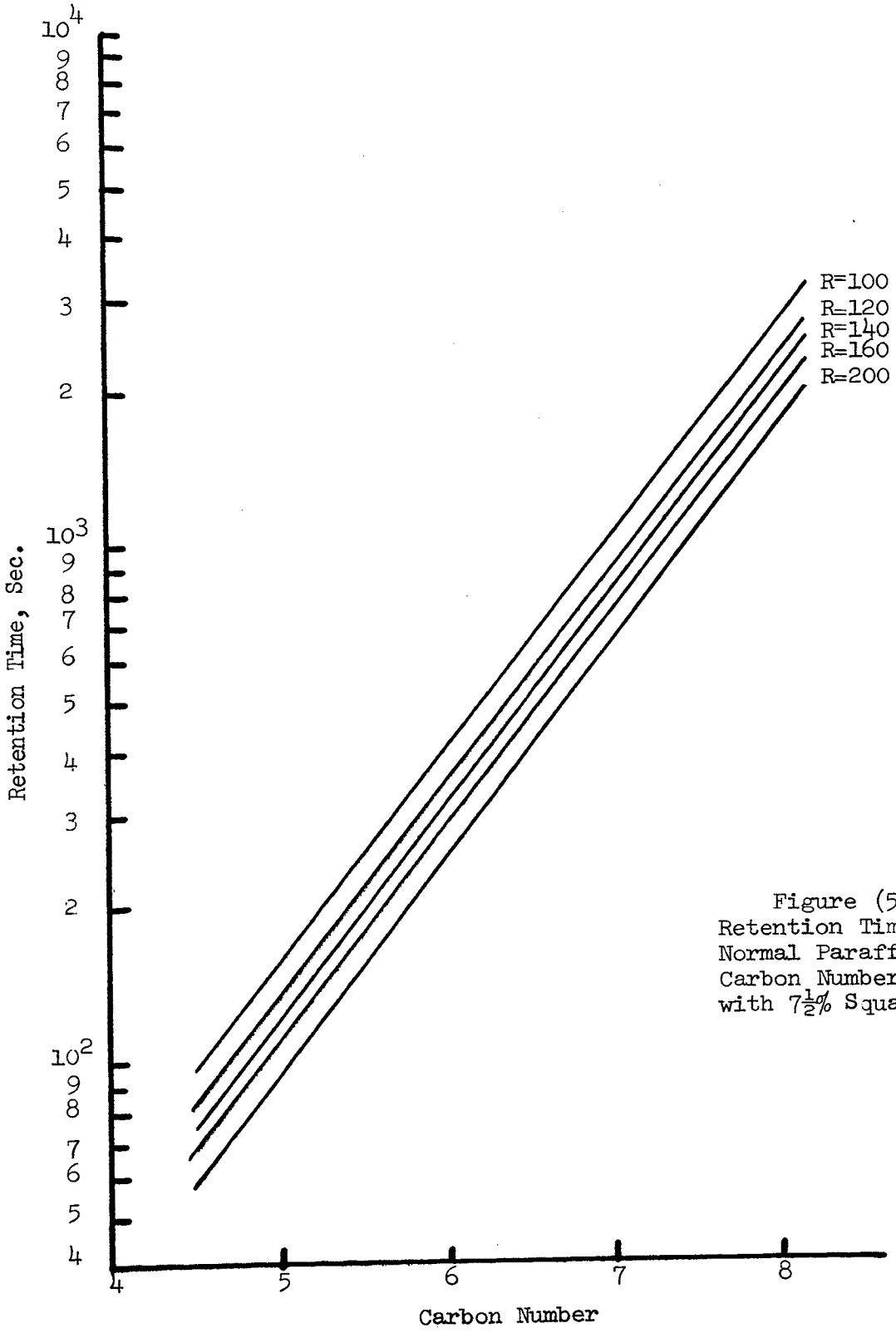

Figure (5)
Retention Time of
Normal Paraffin vs.
Carbon Number at 60°C
with 7½% Squalene Column

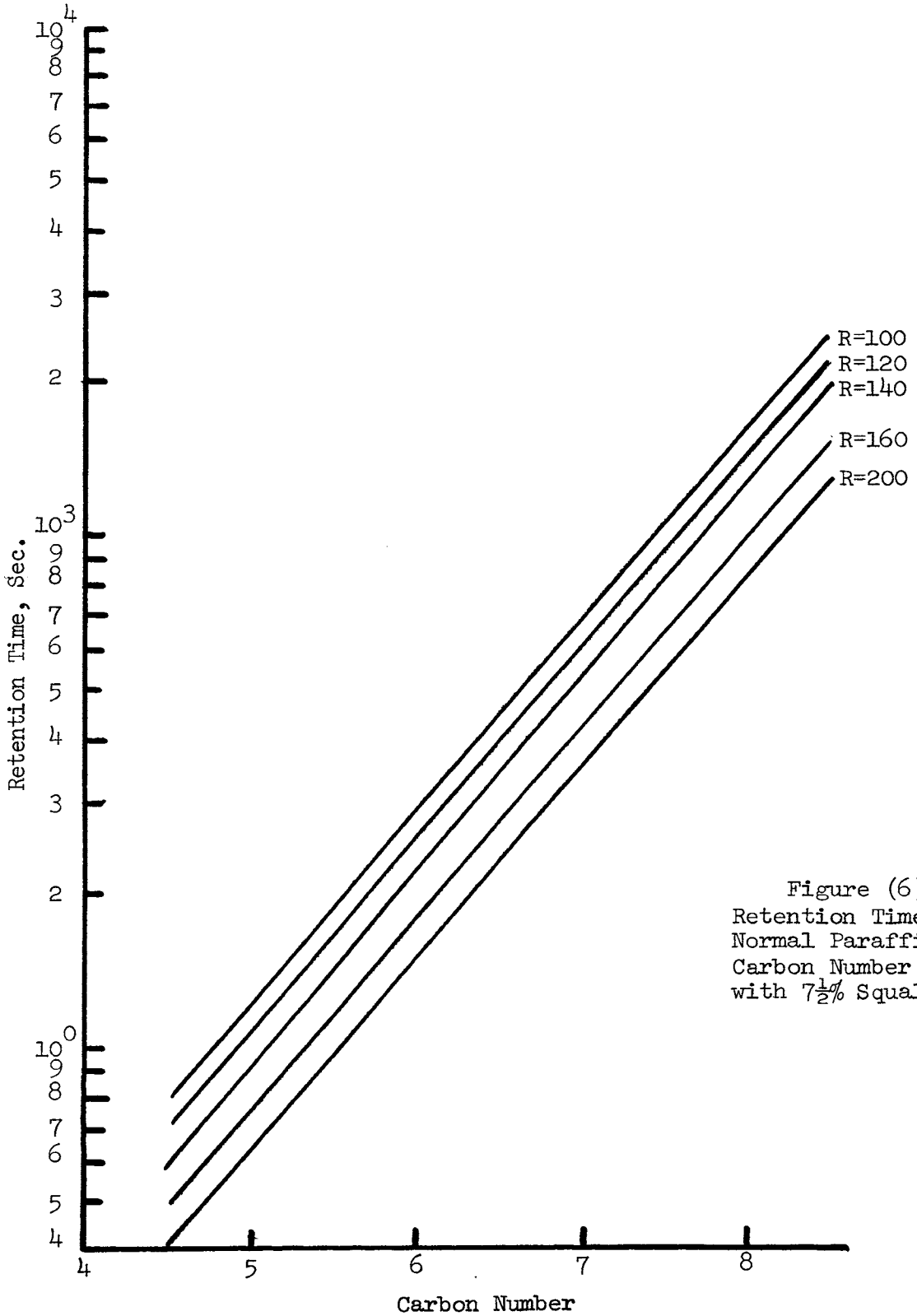

Figure (6)
Retention Time of
Normal Paraffin vs.
Carbon Number at 80°C
with 7½% Squalene Column

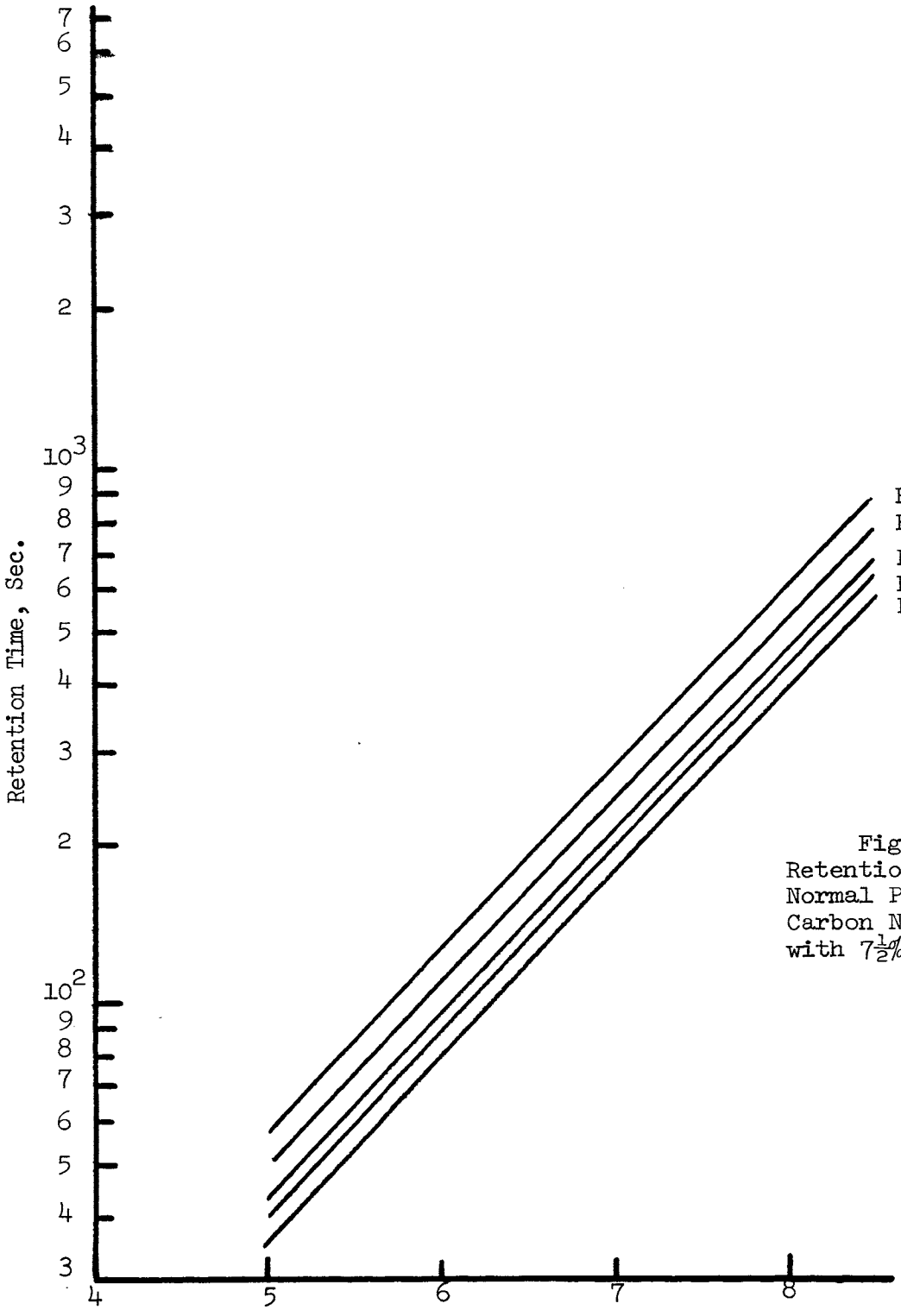

Figure (7)
Retention Time of
Normal Paraffin vs.
Carbon Number at 100°C
with 7½% Squalene Column

The values of 'A', Table 5, when plotted as function of temperature, Figure 8, were obtained.

The values of 'B', Table 6, were found to be constant at a given temperature and independent of the flow rate. By plotting the value of 'B' versus temperature on semilog paper, a series of straight lines resulted that by using ›d of averages could be generalized as Equation 2.

$$B = e^{.257179 - .005083T} \qquad (2)$$

B. Normal Paraffins - T.C.E.P.E. Column

The stationary phase was changed to 10% Tetracyanoethylated Pentaerythritol (T.C.E.P.E.), which restricted the column temperature to a maximum of 150°C.

The data were collected for temperatures of 50,60,70,80,100,110, 120°C, and flow rates of 100,120,140,160,200 for every selected value of temperature. Tables 7 through 13 represent the data, and by plotting the obtained retention time versus carbon number on a semilog paper series of parallel straight lines, Figures 9 through 15, were obtained.

By employing the method of averages, it was attempted to generalize these data in the form of Equation 3.

$$tr = e^{A+BC} \qquad (3)$$

The values of 'A', Table 14, were found to be constant at a given flow rate independent of the temperature and when plotted versus flow rate on a rectangular graph paper, Figure 16 was obtained.

Table 5

Values of 'A' for Normal Paraffin when 7½% squalene was used

Temperature °C	100 cc/min	120 cc/min	140 cc/min	160 cc/min	200 cc/min
50	.2603226	.1310196	-.0091438	-.08976746	-.1953656
60	.2833900	.1408272	.0295105	-.06474686	-.2968712
80	.7261734	.9685898	-.03484344	-.2526779	-.4253159
100	.1593781	.01766205	-.1377144	-.1791153	-.3584671

Table 6

Values of 'B' for Normal Paraffin when 7½% squalene column was used

Temperature °C	'B'
50	1.0080999
60	.9525548
70	.9013622
80	.8583007
100	.7811784

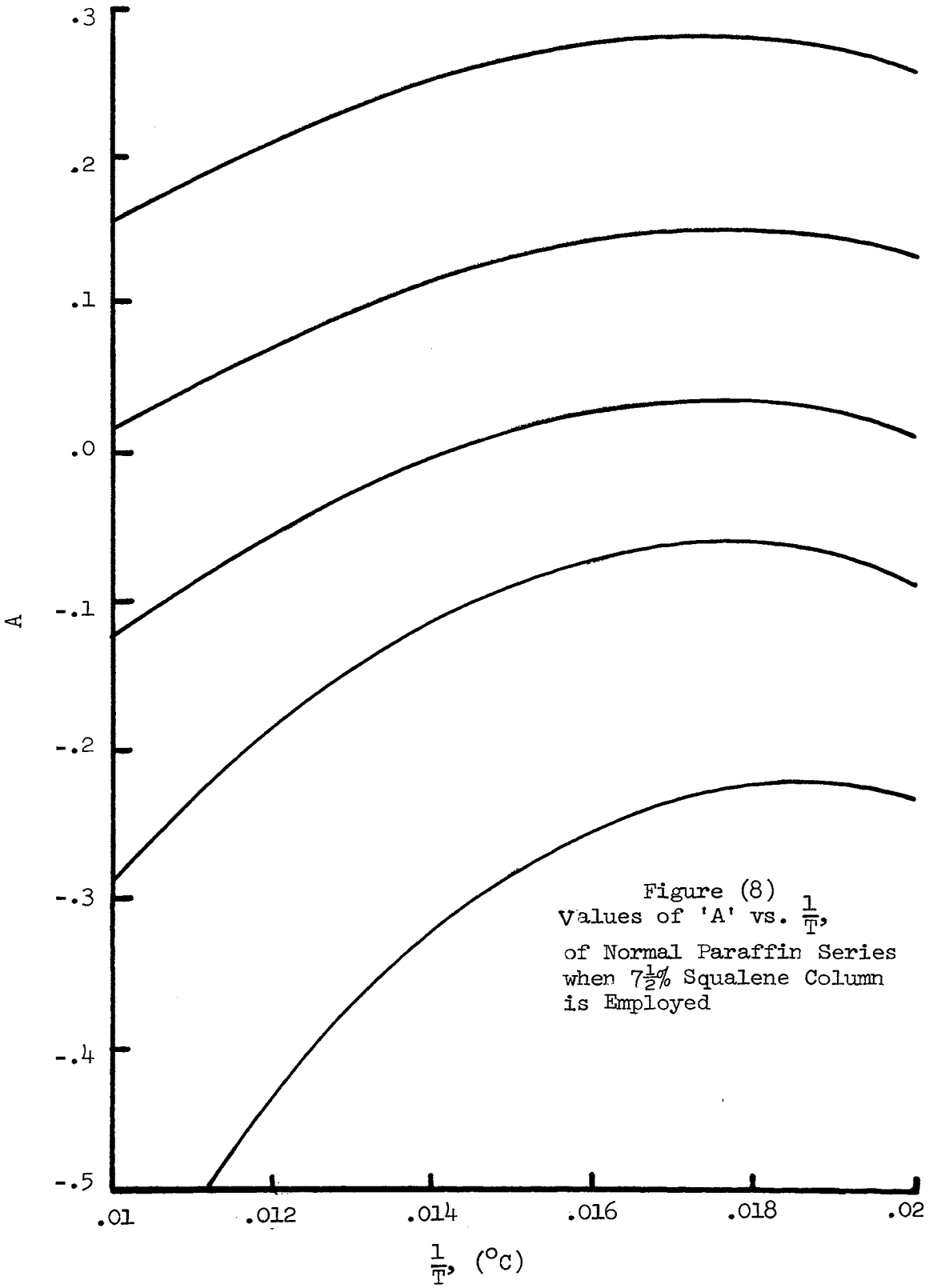

Figure (8)
Values of 'A' vs. $\frac{1}{T}$,
of Normal Paraffin Series
when $7\frac{1}{2}\%$ Squalene Column
is Employed

Table 7

Average Retention at 50°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	43.00	36.20	32.40	28.00	25.60
C_6H_{14}	93.40	83.20	72.20	60.60	56.00
C_7H_{16}	214.40	18.82	161.40	134.40	127.20
C_8H_{18}	455.40	409.4	348.40	287.00	272.80

Table 8

Average Retention at 60°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	32.20	27.60	24.50	22.10	19.00
C_6H_{14}	69.60	60.00	53.10	47.70	41.70
C_7H_{16}	146.20	125.80	111.1	100.00	87.40
C_8H_{18}	307.00	264.10	233.4	210.20	183.70

Table 9

Average Retention Time at 70°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	27.20	22.60	20.45	18.35	15.45
C_6H_{14}	58.30	47.00	42.25	38.20	32.2
C_7H_{16}	117.40	93.95	84.65	76.40	64.35
C_8H_{18}	237.60	189.5	177.50	153.65	129.3

Table 10

Average Retention Time at 80°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	20.80	18.35	16.45	14.60	12.50
C_6H_{14}	41.45	36.95	32.80	28.80	25.10
C_7H_{16}	78.55	69.30	62.50	55.70	48.30
C_8H_{18}	150.05	132.55	119.85	107.10	93.30

Table 11

Average Retention Time at 100°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	15.35	13.35	11.50	10.55	8.72
C_6H_{14}	28.80	25.15	21.70	19.75	16.30
C_7H_{16}	51.20	44.85	38.70	35.00	28.70
C_8H_{18}	91.45	79.95	69.00	62.15	51.38

Table 12

Average Retention Time at 110°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	12.80	11.40	10.05	9.15	7.85
C_6H_{14}	23.05	20.80	18.30	16.6	14.35
C_7H_{16}	39.40	36.05	31.70	28.75	24.90
C_8H_{18}	67.25	62.35	54.95	50.0	43.1

Table 13

Average Retention Time at 120°C

Component	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
C_5H_{12}	11.30	9.90	8.95	8.05	7.0
C_6H_{14}	19.60	17.05	15.60	14.00	11.95
C_7H_{16}	32.75	28.45	26.00	23.40	19.95
C_8H_{18}	54.45	47.45	43.50	39.15	33.4

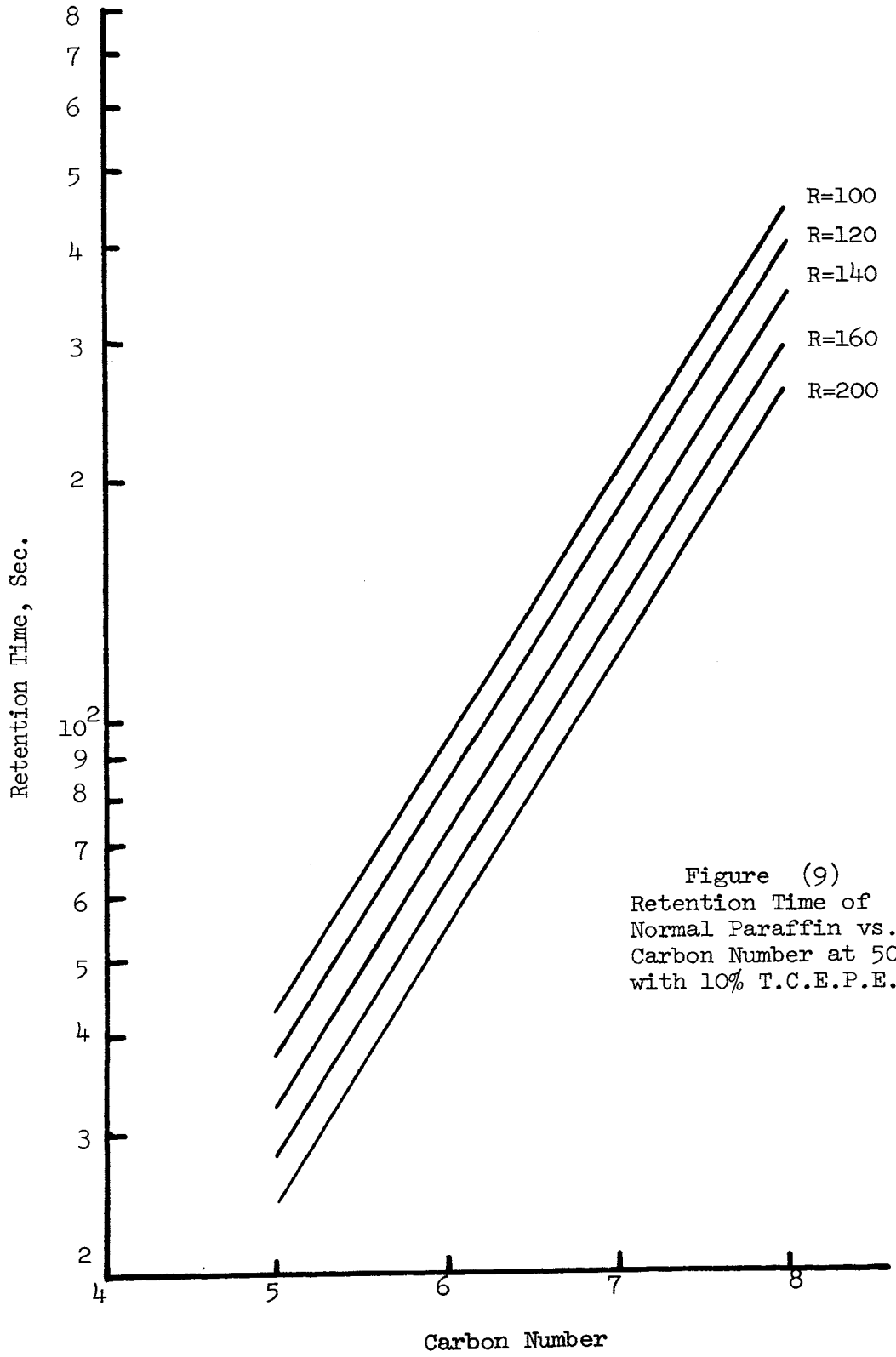

Figure (9)
Retention Time of
Normal Paraffin vs.
Carbon Number at 50°C
with 10% T.C.E.P.E. Column

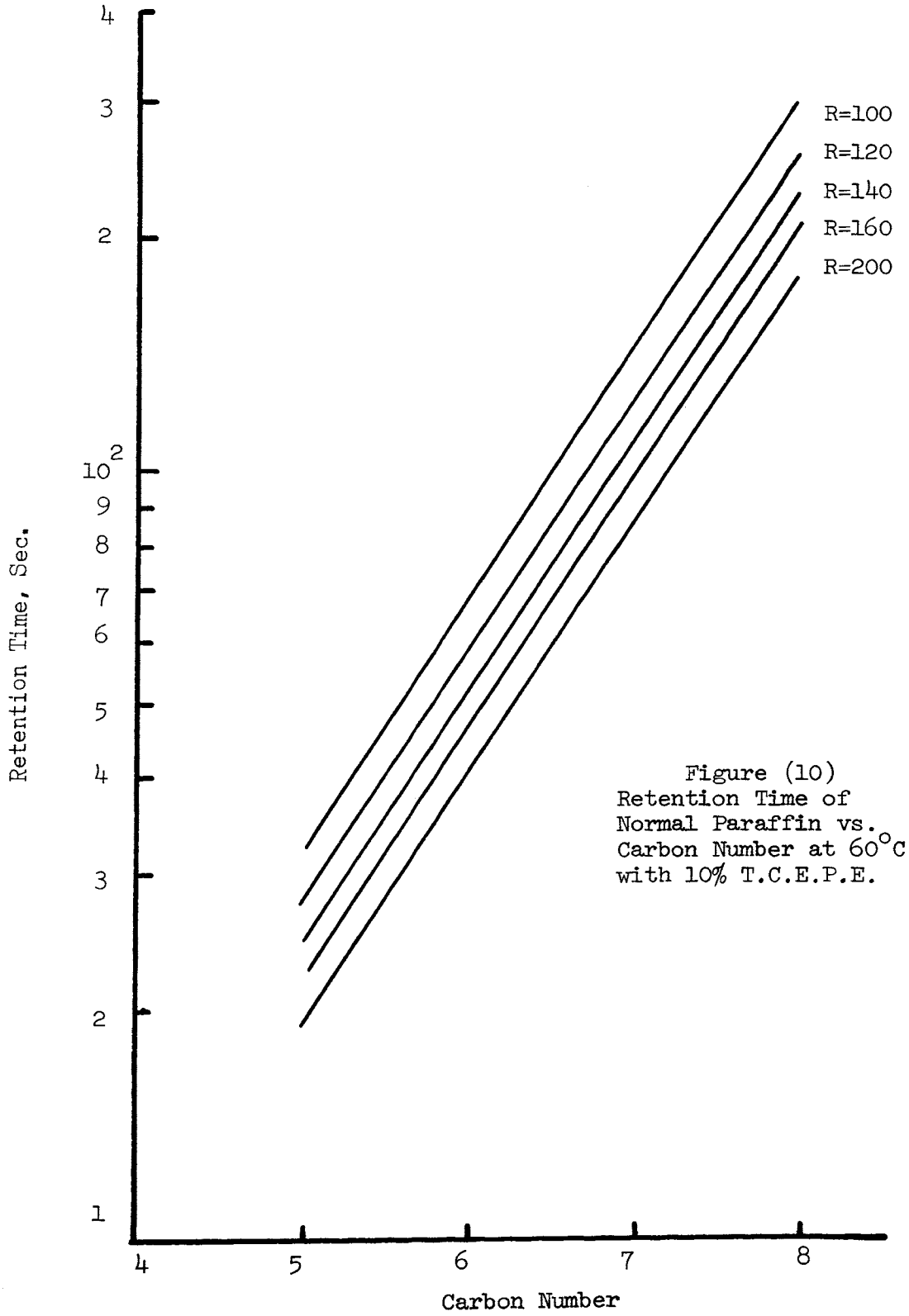

Figure (10)
Retention Time of
Normal Paraffin vs.
Carbon Number at 60°C
with 10% T.C.E.P.E.

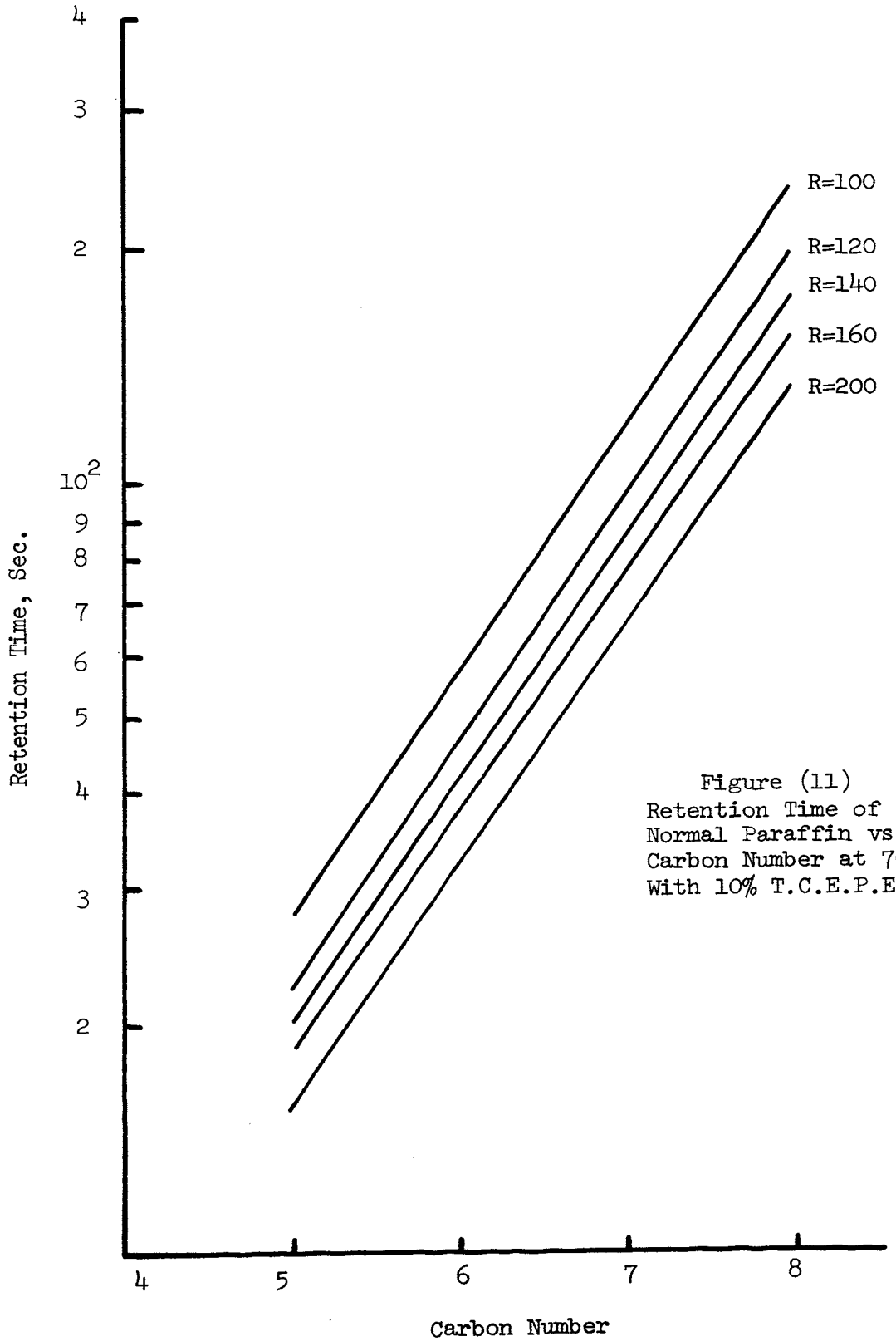

Figure (11)
Retention Time of
Normal Paraffin vs.
Carbon Number at 70°C
With 10% T.C.E.P.E. Column

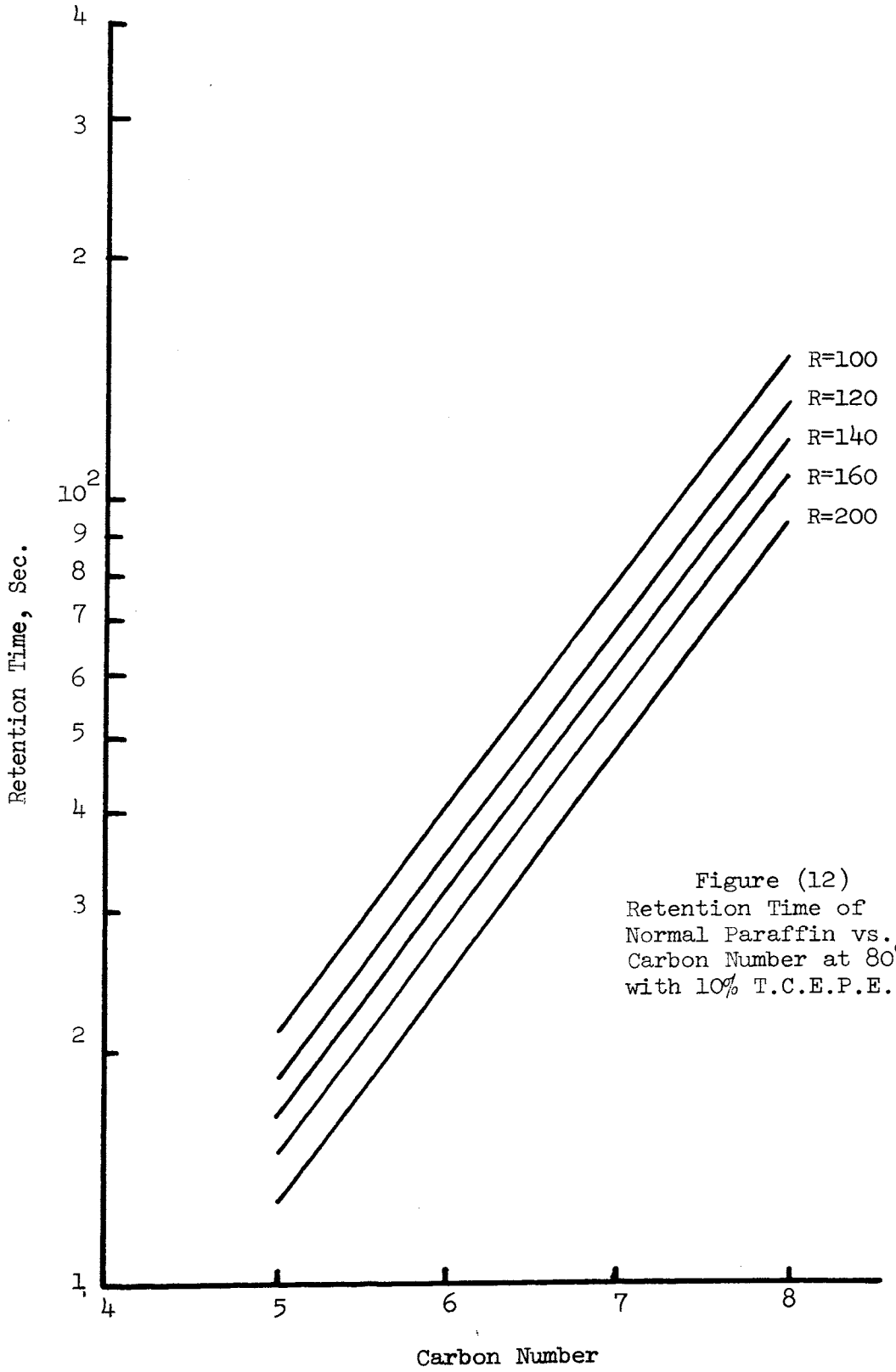

Figure (12)
Retention Time of
Normal Paraffin vs.
Carbon Number at 80°C
with 10% T.C.E.P.E. Column

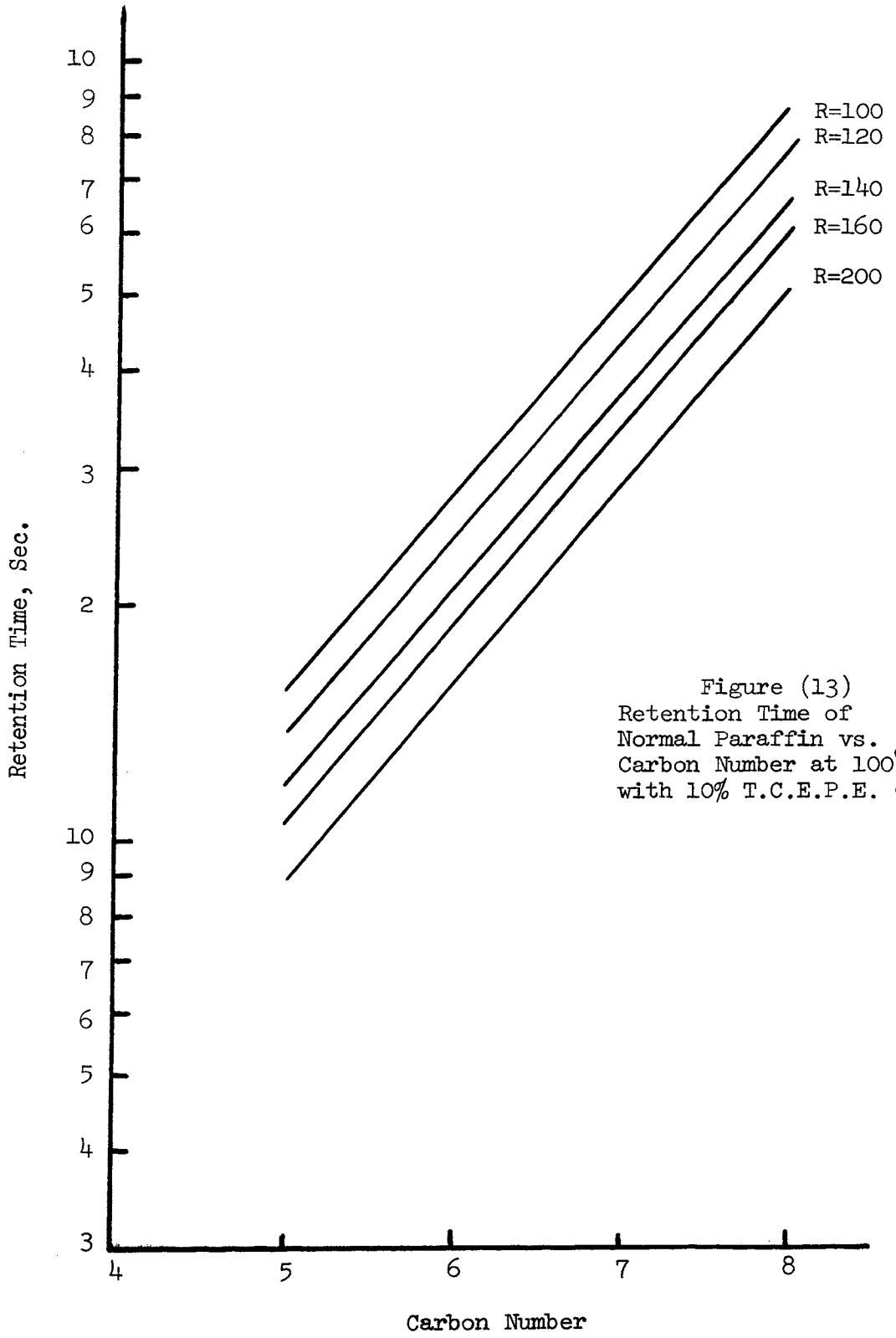

Figure (13)
Retention Time of
Normal Paraffin vs.
Carbon Number at 100°C
with 10% T.C.E.P.E. Column

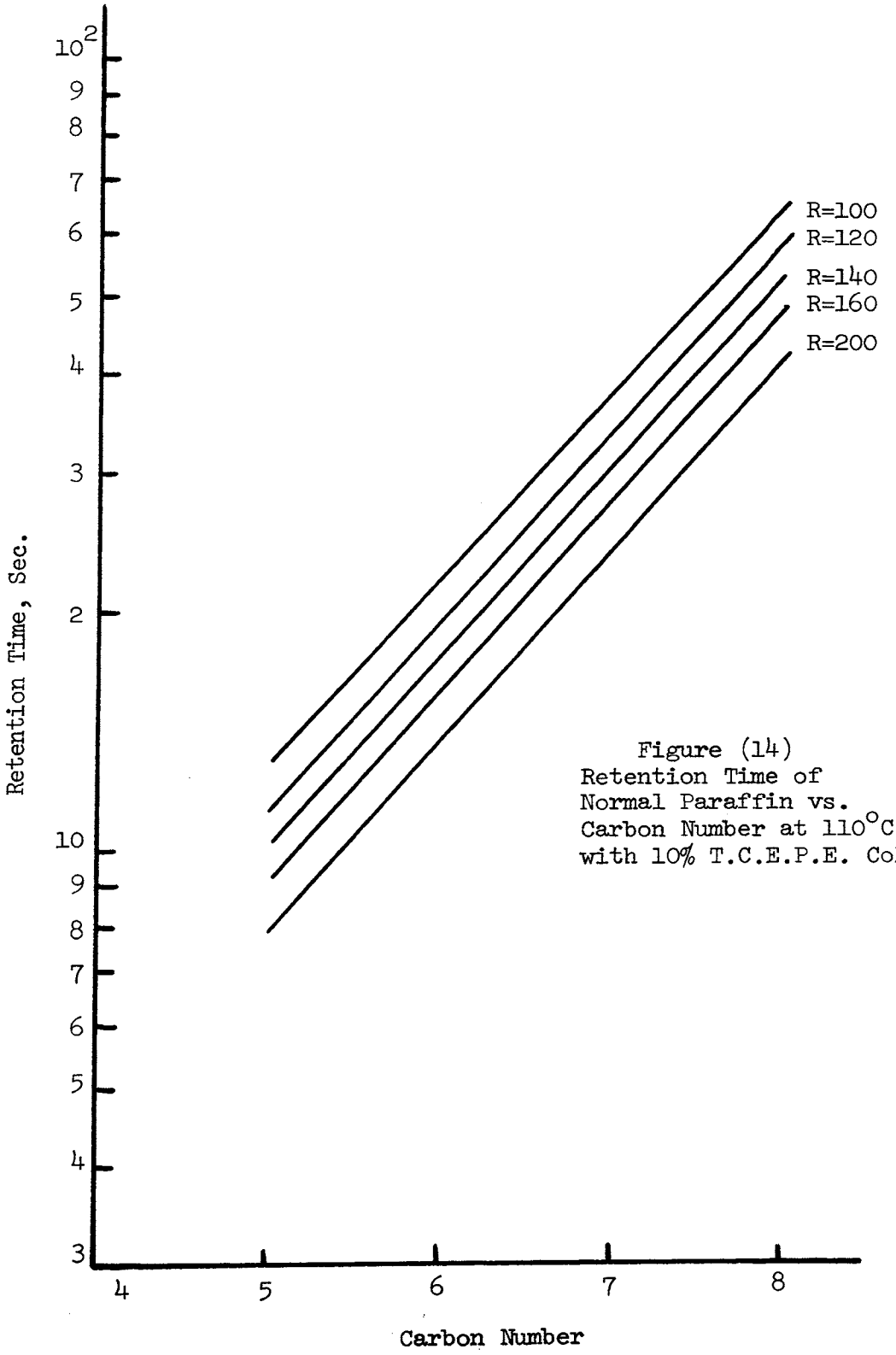

Figure (14)
Retention Time of
Normal Paraffin vs.
Carbon Number at 110°C
with 10% T.C.E.P.E. Column

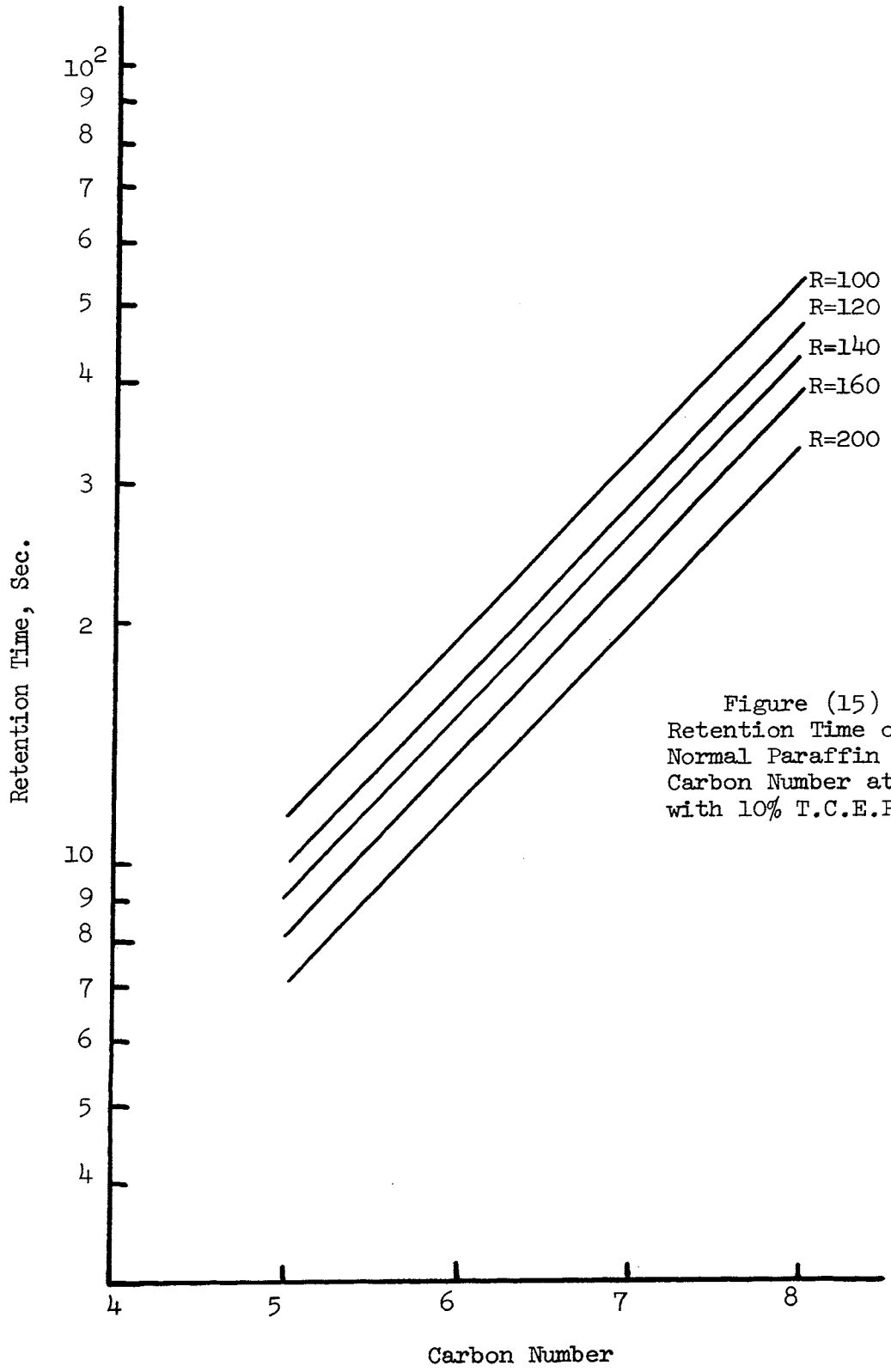

Figure (15)
Retention Time of
Normal Paraffin vs.
Carbon Number at 120°C
with 10% T.C.E.P.E. Column

Table 14

Values of 'A' for Normal Paraffin when 10% T.C.E.P.E. Column was used

Rate cc/min	'A'
100	-.2036257
120	-.3862521
140	-.5058414
160	-.602546
200	-.7841234

Table 15

Values of 'B' for Normal Paraffin when 10% T.C.E.P.E. Column was used

Temperature ^{o}C	'B'
50	.7926269
60	.7513549
70	.7117333
80	.6610595
100	.5977045
110	.5622045
120	.5198876

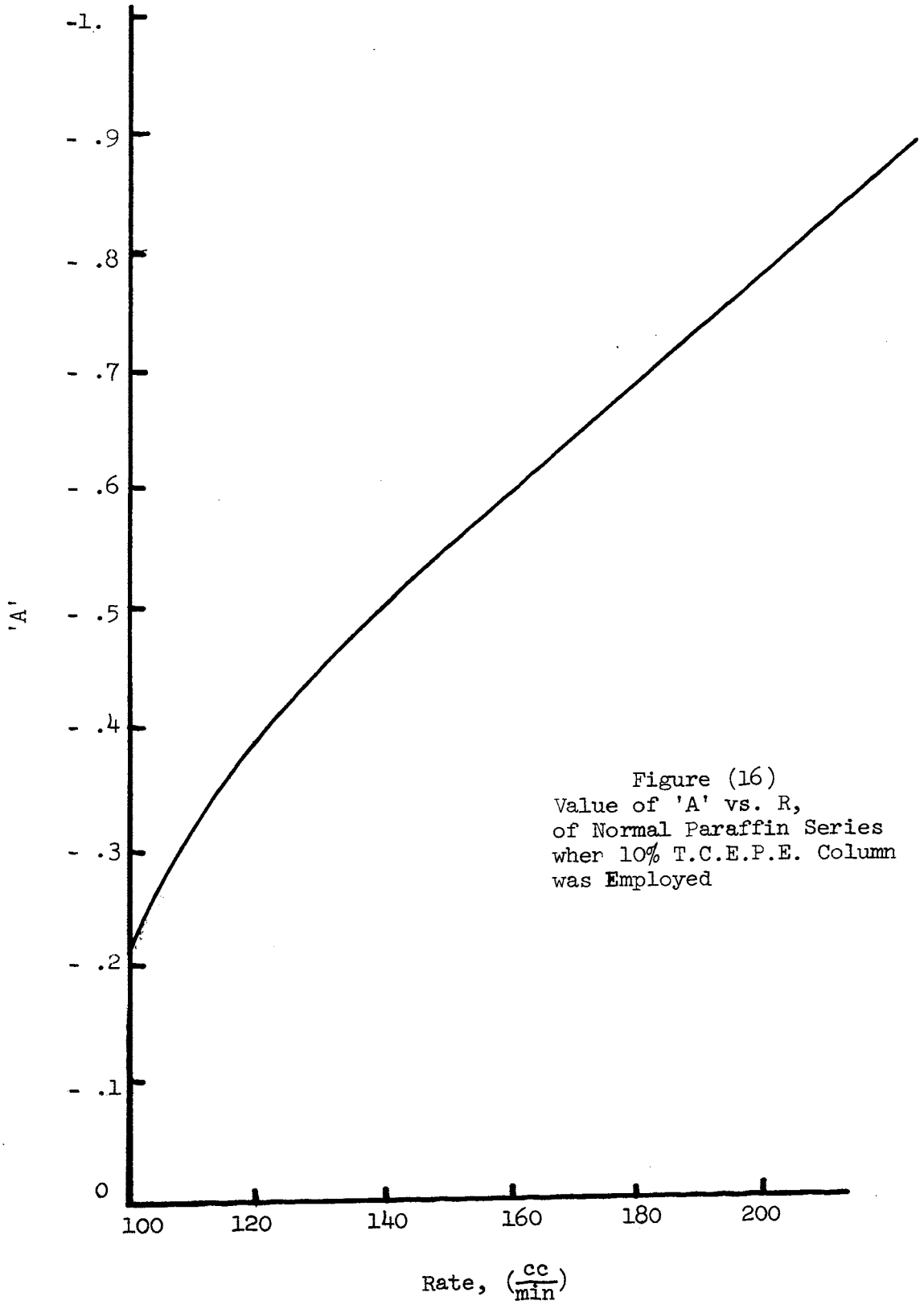

Figure (16)
Value of 'A' vs. R,
of Normal Paraffin Series
wher 10% T.C.E.P.E. Column
was Employed

The values of 'B', Table 15, again were found to be constant at a given temperature for all values of flow rate and when 'B' was plotted versus temperature on a semilog paper, a series of straight lines were obtained which could be represented by Equation 4.

$$B = e^{.070013 - .005950T^{\circ}} \qquad (4)$$

C. Aromatics - T.C.E.P.E. Column

A sample of aromatic compounds consisting of benzene, toluene, and meta-xylene with boiling points of 80.10°, 110.62°, 139.10°C respectively was injected into a T.C.E.P.E. column as suggested by H.M. McNair and E.J. Bonelli[11].

The data were taken when the column temperature remained constant and flow rate was varied from 100 to 200 CC/min., for temperatures of 70 through 120 degree centigrade while the remaining conditions were kept constant as previously explained.

The data are shown in Tables 16 through 20, and are graphically indicated on semilog plots, Figures 17 through 21. All these sets of data may be represented by Equation 5 when the method of averages was used.

$$t_r = e^{A+B^{T_b}} \qquad (5)$$

The values of 'A', Table 21, when plotted versus operating temperatures or flow rate, on a semilog paper yielded a series of parallel straight lines, as shown on Figures 22 and 23. However, a general equation, in the form of Equation 6 and 8 using method of averages was determined.

$$A = e^{a_1 - .004284T} \tag{6}$$

where; $a_1 = e^{.7116249 - .0006228R}$, (7)

or; $A = e^{a_2 - .0012035R}$, (8)

and, $a_2 = e^{.7328444 - .0025882T}$. (9)

The values of 'B', Table 22, were found to be function of temperature again, and when plotted versus temperature on a semilog paper, a series of straight, parallel lines were obtained, which by using method of averages, could be represented by Equation 10.

$$B = e^{3.501611 - .005099T} \tag{10}$$

Table 16

Average Retention Time at 70°C

Compound	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
Benzene	879.0	735.0	645	591	50.4
Toluene	1680.0	1395.0	1215	1119	951
Metaxylene	2937.0	2598	2259	2070	1764

Table 17

Average Retention Time at 80°C

Compound	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
Benzene	607.2	537.6	474.0	434.4	362.4
Toluene	1105.2	984.0	861.6	794.4	661.2
Metaxylene	1974.0	1762.8	1533.6	1420.8	1183.2

Table 18

Average Retention Time at 100°C

Compound	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
Benzene	367.2	322.8	283.2	255.6	221.4
Toluene	633.6	556.8	489.6	441.0	380.4
Metaxylene	1070.4	940.8	828.6	746.6	643.8

Table 19

Average Retention Time at 110°C

Compound	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
Benzene	285.6	246.6	219.0	202.8	168.0
Toluene	479.4	412.8	366.6	336.0	282.0
Metaxylene	787.8	680.4	603.6	553.2	460.2

Table 20

Average Retention Time at 120°C

Compound	Ave. Ret. Time at 100 cc/min	Ave. Ret. Time at 120 cc/min	Ave. Ret. Time at 140 cc/min	Ave. Ret. Time at 160 cc/min	Ave. Ret. Time at 200 cc/min
Benzene	223.2	198.0	176.4	161.2	140.8
Toluene	364.8	324.0	288.8	264.4	229.2
Metaxylene	585.6	521.2	465.2	425.2	368.4

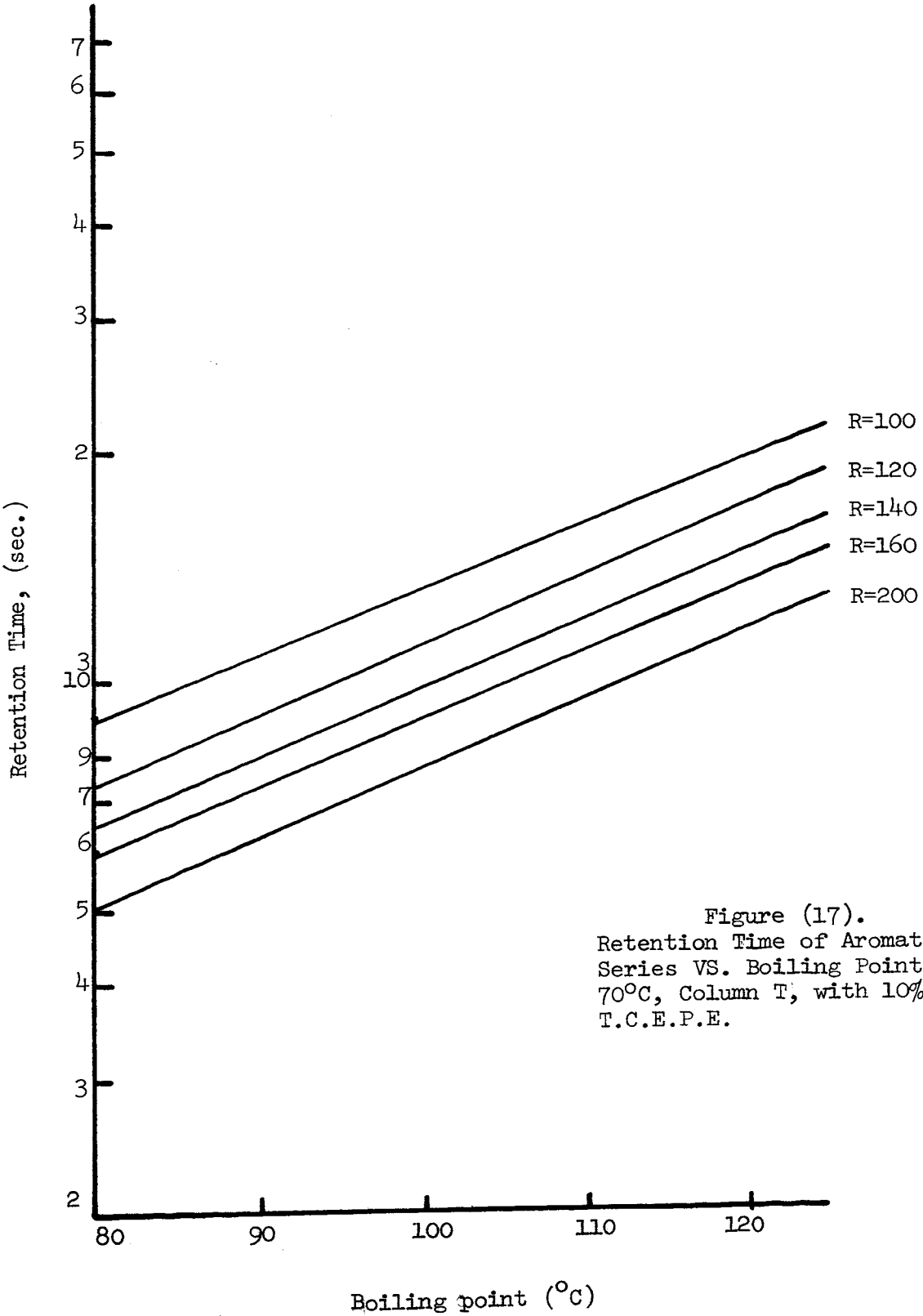

Figure (17).
Retention Time of Aromatic Series VS. Boiling Point at 70°C, Column T, with 10% T.C.E.P.E.

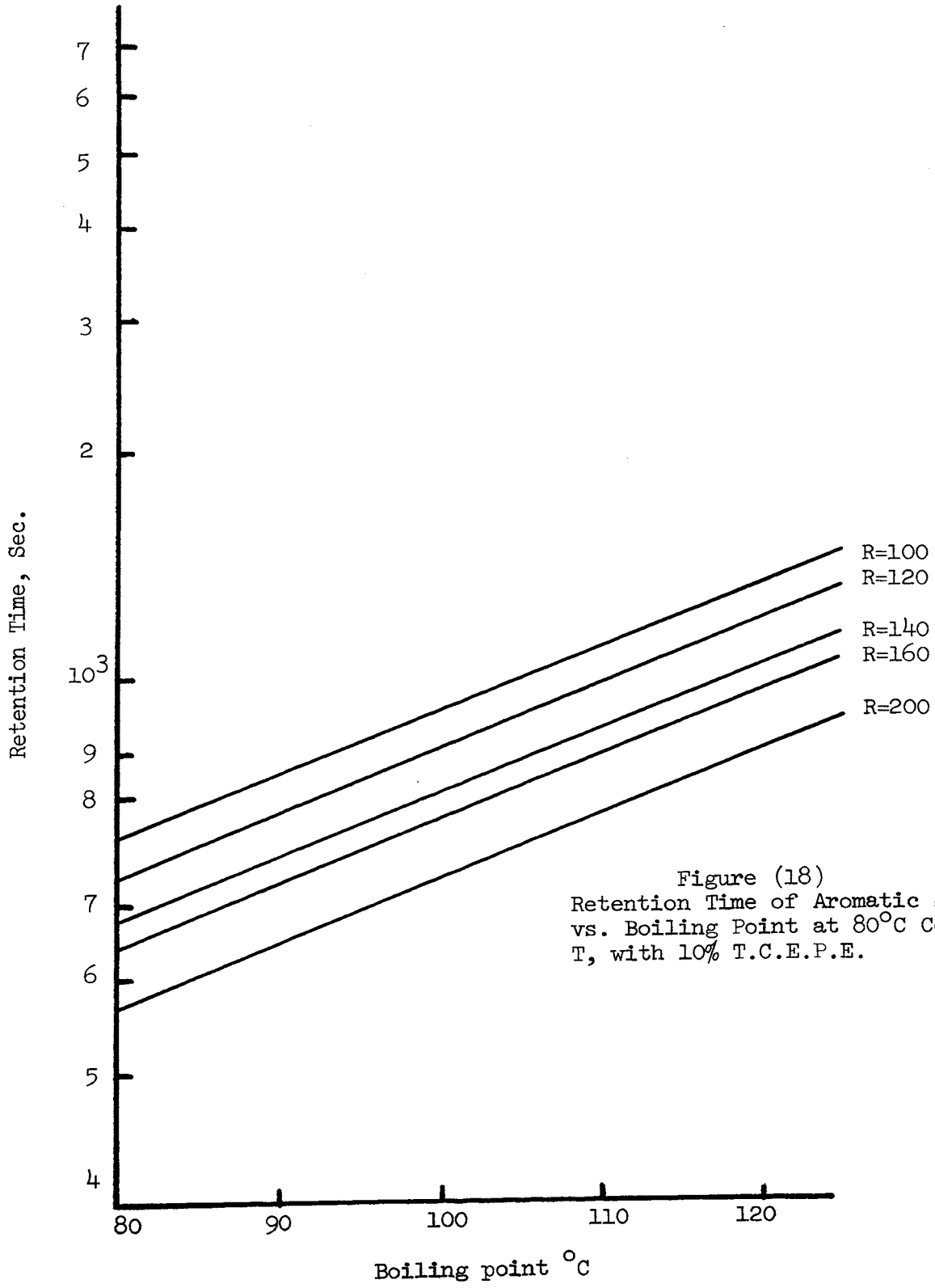

Figure (18)
Retention Time of Aromatic Series vs. Boiling Point at 80°C Column T, with 10% T.C.E.P.E.

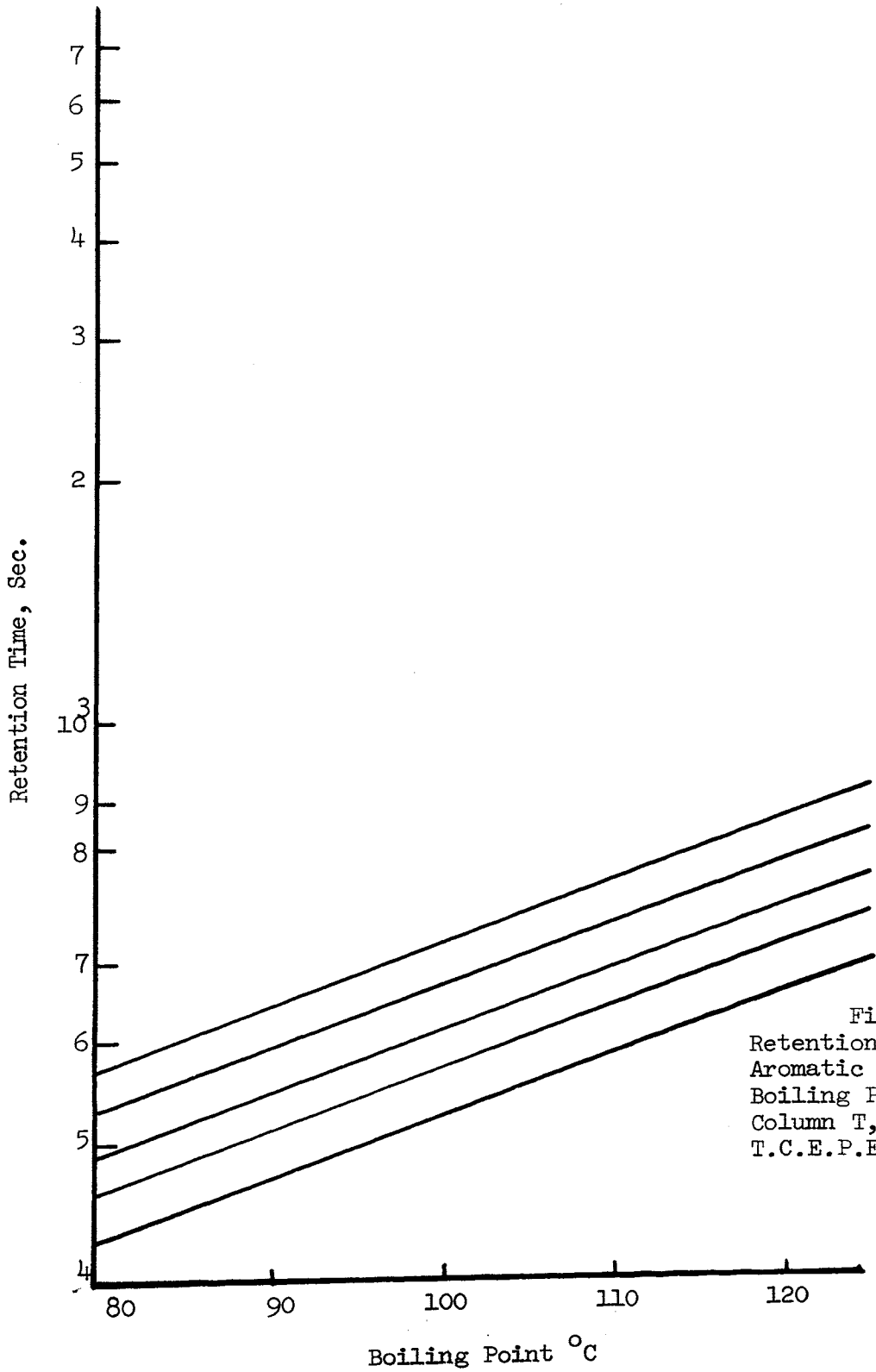

Figure (19)
Retention Time of Aromatic Series vs. Boiling Point at 100°C Column T, with 10% T.C.E.P.E.

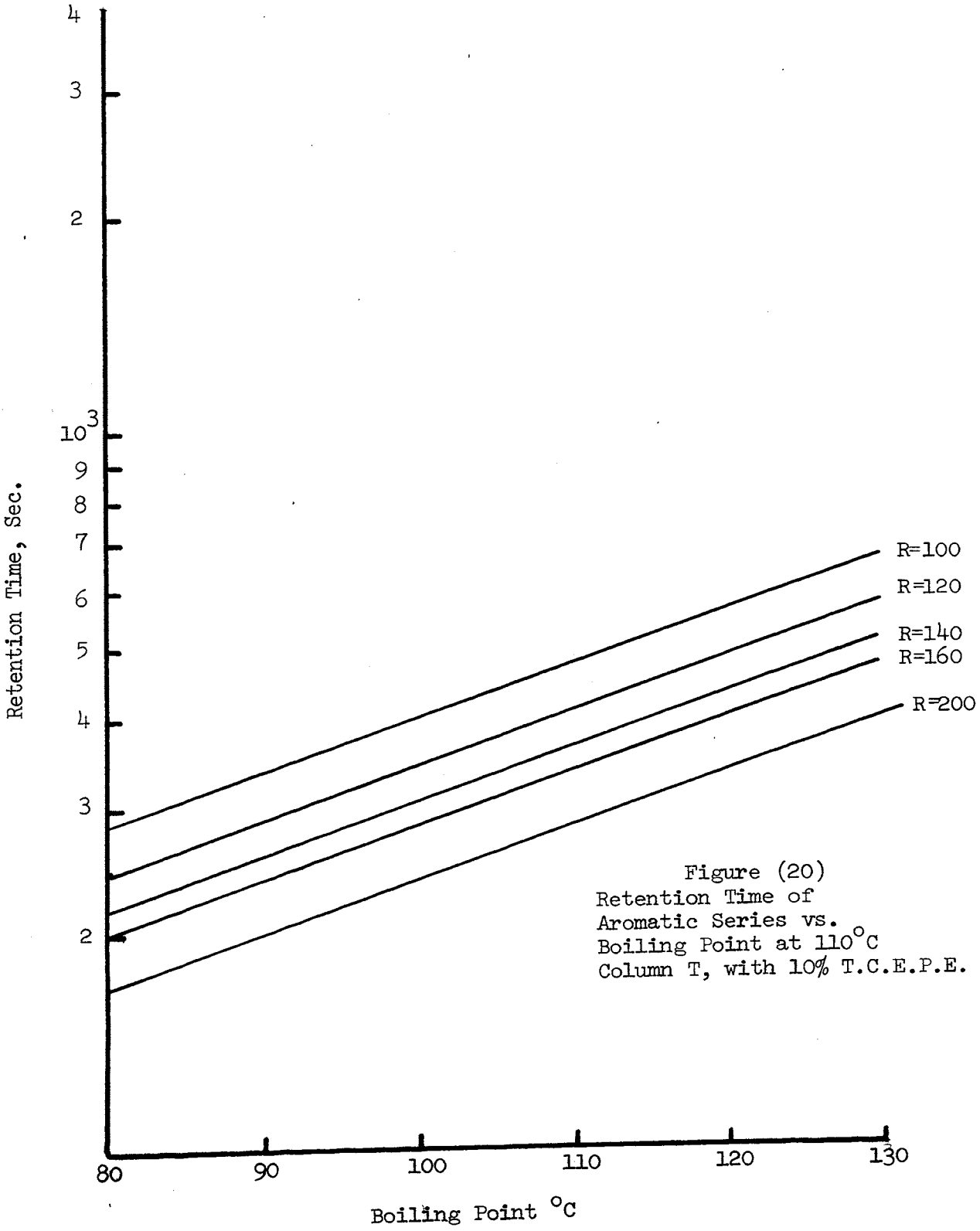

Figure (20)
Retention Time of
Aromatic Series vs.
Boiling Point at 110°C
Column T, with 10% T.C.E.P.E.

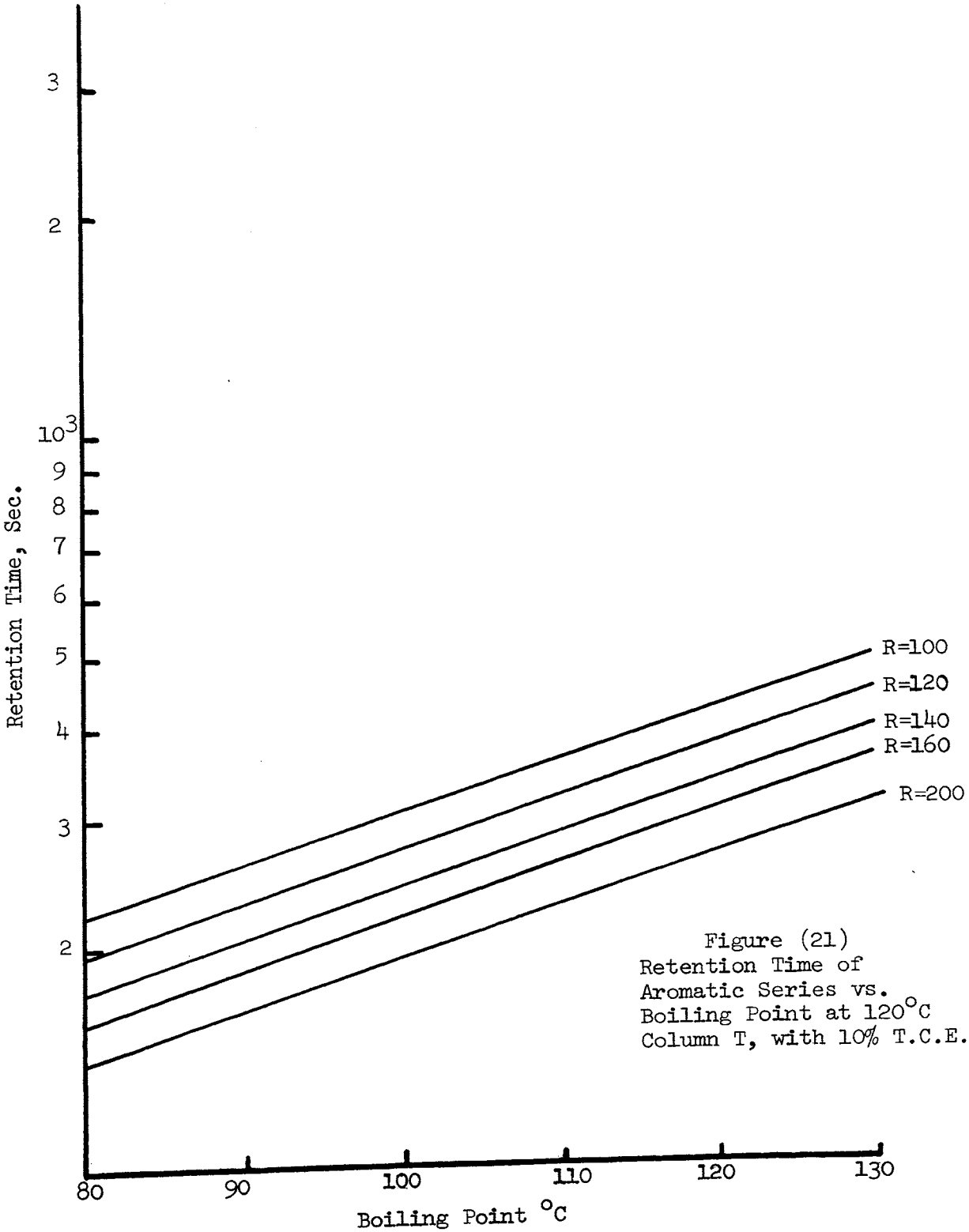

Figure (21)
Retention Time of
Aromatic Series vs.
Boiling Point at 120°C
Column T, with 10% T.C.E.P.E.

Table 21

Values of 'A' for Aromatic Compounds when 10% T.C.E.P.E. was used

Rate cc/min	Temperature 70°C	80°C	100°C	110°C	120°C
100	5.147818	4.805094	4.450957	4.27506	4.096349
120	4.881986	4.672043	4.322408	4.127077	3.971876
140	4.763138	4.564278	4.186255	4.009913	3.853610
160	4.677105	4.462352	4.07996	3.945662	3.763772
200	4.517874	4.283141	3.947635	3.754854	3.63854

Table 22

Values of 'B' for Aromatic Compounds when 10% T.C.E.P.E. was used.

Temperature	Value of 'B'
70	.02111265
80	.02002655
100	.018153780
110	.017131096
120	.01638315

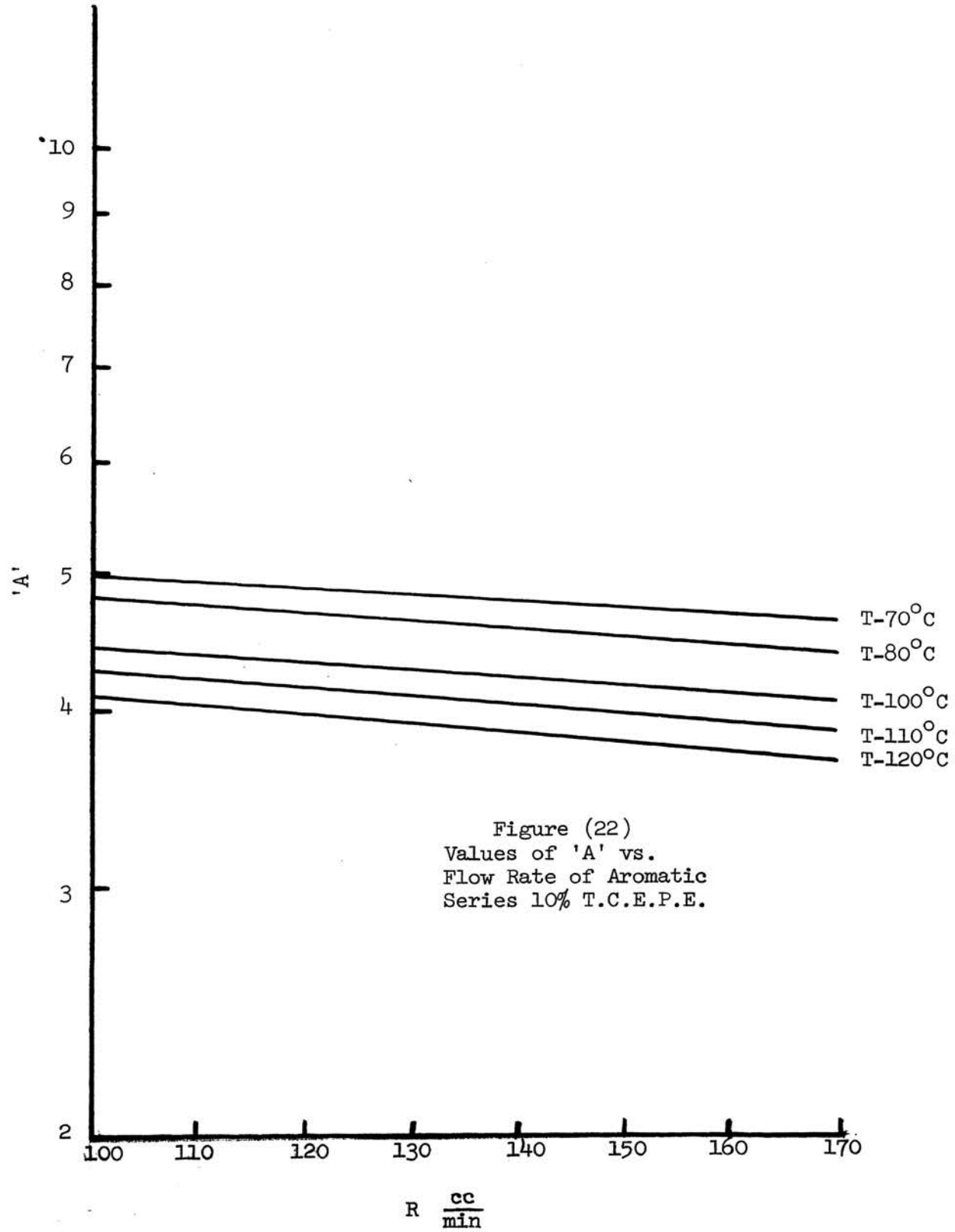

Figure (22)
Values of 'A' vs.
Flow Rate of Aromatic
Series 10% T.C.E.P.E.

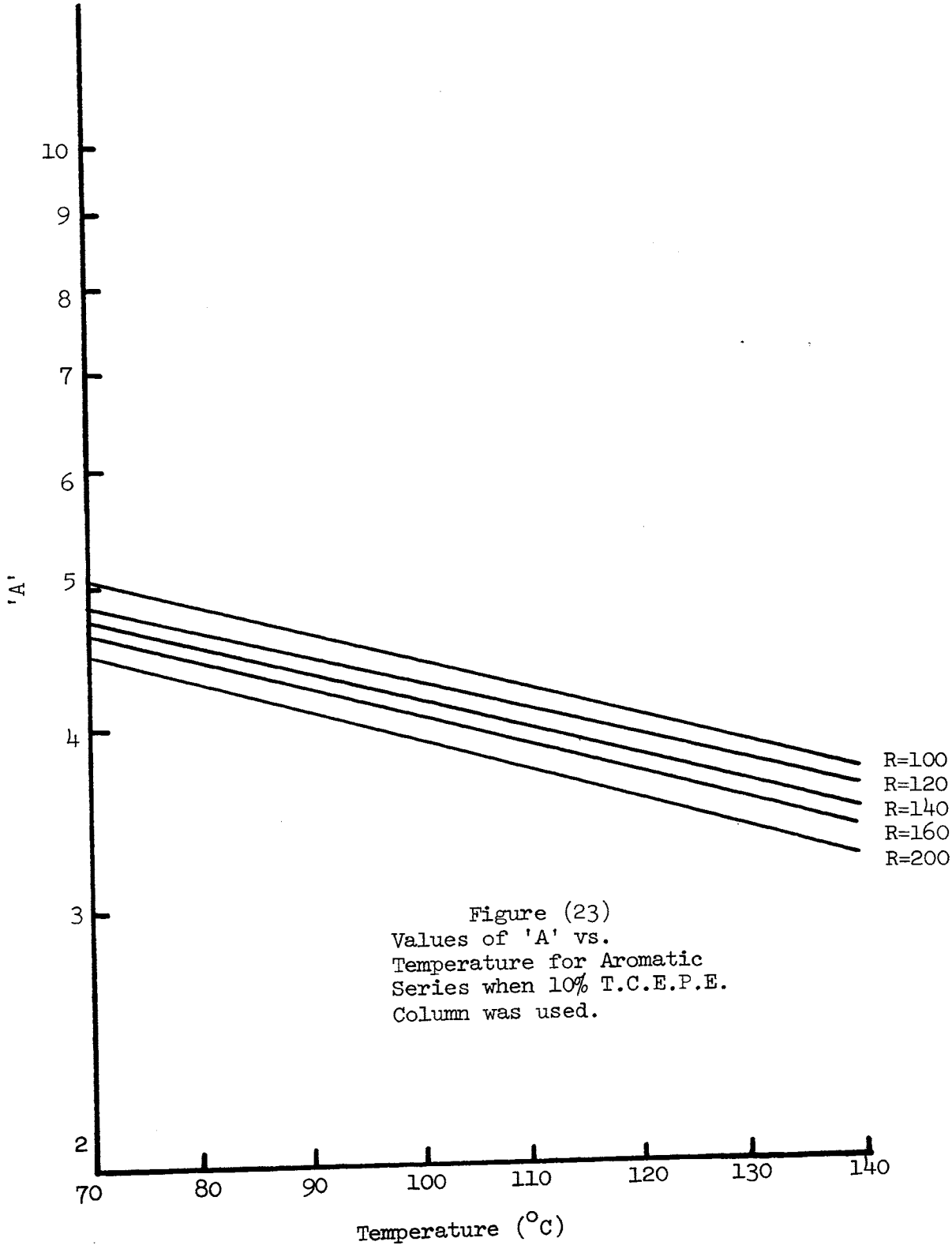

Figure (23)
Values of 'A' vs.
Temperature for Aromatic
Series when 10% T.C.E.P.E.
Column was used.

V. UNKNOWN DETERMINATION

A sample of regular gasoline was injected into the gas chromatograph under the same experimental condition as before. The column used in this part was a 7½% squalene, the same column which was used in the first part of the experiment, at 100°C. The operating flow rate was chosen to be 120 CC/min. Several peaks were obtained and when Figure 7 was employed the presence of C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$ was confirmed. The values of their retention times were found to be 21, 50.1, 110, 236, 530, 1130, and 2550 seconds respectively.

The same results were obtained when Equation 2 was used.

$$tr = e^{A+BC}$$

The value of 'A' was found from Figure 8.

$$A = .01766$$

The value of 'B' was found from Equation 3.

$$B = e^{.257179 - .005083*100^{\circ}}$$

$$B = .78117$$

solving the Equation 2 for C_i,

$$C_i = \frac{Ln(t) - .01766}{.78117}$$

4,5,6,7,8,9,10 were the answers, matching with the results obtained from the Figure 7. Other peaks that were present, did not give round numbers for the value of C and there was no indication of aromatic compounds.

In the second part, a T.C.E.P.E. column was used, the same column employed in the second and third parts of the experiment. The column temperature was set at 120°C and the flow rate of 120 CC/min was selected for this separation. Other experimental conditions being the same as previously explained, several peaks in the normal paraffin range appeared, of which the following were identification when Figure 15 was used, C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$ with the retention time of 15.9, 26.8, 76.5 and 130 respectively. The same results were obtained when Equation 2 was employed.

$$tr = e^{A+BC}$$

The value of 'A' was found to be -.38625 from Figure 16, and 'B' was found from Equation 4,

$$B = e^{.070013 - .00596*120^{\circ}}$$

solving the Equation 2 for C

$$C = \frac{Ln(t) + .3862521}{.525}$$

6,7,9,10 were the results which match with the obtained results when Figure 15 was used.

It could be readily seen that not all the normal paraffin could be detected by a T.C.E.P.E. column, for the peaks were very close together.

In the aromatic range, boiling points of all the peaks were attempted to be ascertained through employment of retention times, and by means of their boiling point, to identify the nature of the compound.

Equation 5 was employed to calculate the boiling points of compounds,

$$tr = e^{A+B\,T_b}$$

where 'A' found to be 3.971876 using Figure 22 or 23, and 'B' found to be .0164 using Equation 10.

Solving the Equation 5 for t_o,

$$T_b = \frac{Ln(t) - 3.971876}{.0164} .$$

It was found that several peaks had comparatively close boiling points to the boiling points of the aromatic compounds as shown in Table 23. The same results were obtained when Figure 21 was employed.

Table 23 List of Aromatic Compounds Present in the Sample of Regular Gasoline as Determined with the Aid of 7½% Squalene and 10% T.C.E.P.E. Columns

Retention time	Calculated °C boiling point	Closest boiling point °C to the unknown	Name of the unknown
207	86.8	80.10	Benzene
328	112.9	110.62	Toluene
483	136.5	136.19	Ethylbenzene
520	141.1	139.10	m-xylene
680	157.2	159.22	n-propylbenzene
744	162.9	161.99	1-Methyl-4-ethylbenzene
810	168.0	169.12	Tert-Butylbenzene
929.2	176.4	176.08	1,2,3-Trimethylbenzene
1032	182.9	183.27	n-Butylbenzene
1119.4	187.8	188.20	1-3-Dimethyl-4-ethylbenzene
1247	194.3	193.91	1,2-Dimethyl-3-ethyl-benzene
1393	201.0	188.00	1,2,3,5-Tetramethylbenzene
1459	202.0	204.10	1-Methyl-3-n-butylbenzene
1595	209.0	208.50	1-2-Dimethyl 1-4-n-propylbenzene

VI. SUMMARY AND CONCLUSIONS

The purpose of this program was to investigate whether homologous compounds, in general, elute in a regular sequence. It was found that the plot of logarithm of retention time versus number of carbon atoms for a normal paraffin group was a straight line, and shifts depending the operating temperature and flow rate were noted. The investigation was performed with both $7\frac{1}{2}\%$ squalene and 10% T.C.E.P.E. columns.

A similar retention was obtained when the logarithm of retention time versus the boiling point of aromatic compounds was plotted. This was obtained with a 10% T.C.E.P.E. column, recommended for aromatic compounds and again, the lines shifted depending on the operating temperature and flow rate.

From the results obtained, it was concluded that log of retention time was proportional to any increasing property of a homologous series.

It was also intended to develop general equations to represent these obtained straight lines. Method of averages was employed and equations of type $t = e^{A+BX}$, were found, where 'X' could be any increasing property of the homologous series, in this case carbon number and t was the registered retention time on the recorder. The values of 'A' normal paraffin series, were shown on Figure 8 when $7\frac{1}{2}\%$ squalene was used and on Figure 16 when 10% T.C.E.P.E. column was used. The values of 'B', using method of averages, were found to be a function of temperature only and could be represented as

$$B = e^{.257179 - .005083T} \text{ with } 7\tfrac{1}{2}\% \text{ squalene column,} \qquad (2)$$

and,

$$B = e^{.070013 - .00596T} \text{ with 10\% T.C.E.P.E. column} \tag{4}$$

For aromatic compounds, the same type of equation was developed with retention time as a function of boiling point, ^{o}C, of the compound.

$$tr = e^{A+BT_b} \tag{5}$$

The values of 'A' in this case were shown on Figure 22 or 23. It was also found that 'A' itself could be represented as follows:

$$A = e^{a_1 - .004284T}, \tag{6}$$

$$A = e^{a_2 - .001203521R}, \tag{8}$$

where;

$$a_1 = e^{.7116249 - .000622814R}, \tag{7}$$

$$a_2 = e^{.7328444 - .002588203T}. \tag{9}$$

The values of 'B' using the method of averages were found as;

$$B = e^{-3.501611 - .005099472T}. \tag{10}$$

In a final analysis, a sample of regular gasoline was injected into the chromatograph to identify its constituents. It was found to be easier to identify normal paraffin compounds when a $7\frac{1}{2}\%$ squalene column was used and aromatic compounds when a 10% T.C.E.P.E. column was employed, as expected. Several of the identified constituents were presented on pages 52, 53, 54, and Table 17. A complete analysis of gasoline, however requires the development of the same technique

described in this paper for isomers of the normal paraffins, the cyclic hydrocarbons, and the naphthenes.

VII. APPENDICES

APPENDIX A

Nomenclature

Q = flow rate, $\frac{ml}{min}$.

tr = retention time, sec.

C = carbon number in a normal parafin compound.

T = temperature, degrees centigrade.

T_b = boiling point of a compound, degrees centigrade.

e = 2.71828

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IX VITA

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